# Lawrence Berkeley Laboratory
## UNIVERSITY OF CALIFORNIA

# ENERGY & ENVIRONMENT DIVISION

OIL SHALE RESEARCH

Chapter from the Energy and Environment
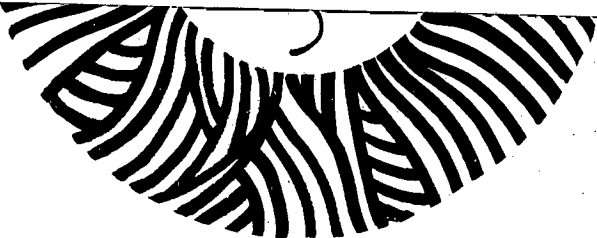Division Annual Report 1978

August 1979

# DISCLAIMER

# OIL SHALE RESEARCH

chapter from
Energy & Environment Division
Annual Report 1978

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OIL SHALE RESEARCH

Vast resources of oil shale — in excess of 1.8 trillion barrels of oil — exist in the tri-state area of Colorado, Utah and Wyoming. Some 80 billion barrels of this oil is recoverable with technology available today — more energy than is contained in all of the known oil and gas reserves in the United States. The U.S. Department of the Interior has estimated that with more advanced technology and under different economic conditions, oil shale deposits in the U.S. might yield as much as 800 billion barrels of oil.

Oil shale is a layered, greyish, sedimentary rock that was deposited eons ago in fresh water lakes. It contains about 20% organic material, primarily kerogen, which originated from algae and other microorganisms and wind-blown or water-borne pollen and spores. The inorganic material is a dense, tough marlstone composed primarily of the two carbonaceous minerals, dolomite and calcite. The shale may exist anywhere from 100 to 3000 feet beneath the surface interbedded with varying amounts of tuff, siltstone, sandstone and claystone and laced with groundwater aquifers.

Oil may be extracted from the shale by heating the rock to break down the kerogen, a high molecular weight polymer, into smaller molecules. This process, termed pyrolysis, may be carried out in a surface retort or in the ground (in-situ processes). The technology for surface retorting is further advanced but is limited by economic and environmental factors. Large volumes of rock must be mined, crushed, transported, and disposed of. The processing requires large volumes of water and generates large quantities of noxious gases. In the in-situ processes, the majority of the resource is pyrolyzed in the ground (a small amount, usually about 20%, is removed to create void space). This approach to processing oil shale is presently under intensive study by industry and the Department of Energy as an economic and environmentally superior alternative to surface processing.

The existence of these rich Rocky Mountain oil shale deposits has been known for more than sixty years, and the exploitation of them has been considered, off and on, from just about every conceivable angle — technologically, economically, politically, and most recently, environmentally.

The Oil Shale Program at the Lawrence Berkeley Laboratory is concerned with the environmental aspects of oil shale production — air, solid waste and water problems — of far reaching consequences. The program has identified a number of previously unrecognized or little understood environmental concerns — in situ leaching, air emission of toxic trace elements, aqueous effluent disposal — and is conducting basic and applied research in these areas. The goal of the program is to develop the scientific information necessary to understand and, ultimately, to control environmental problems.

Information on the chemical composition of oil shale and its by-products is being developed to assess environmental impacts and to select and develop suitable control strategies. Lawrence Berkeley Laboratory is characterizing the gases, oils, waters, and solids produced by oil shale retorting. Methods are being developed to measure organometallic and organic compounds present in aqueous effluents and to assess their impact on aquatic biota. In-depth geochemical investigations of the Green River Formation are being conducted which indicate that there is signficant variability in the concentration of trace elements vertically through the oil shale formation. Detailed elemental mass balances have been completed on some 30 runs of several pilot-scale retorts, and the effect of retort operating conditions on trace element distribution is being investigated.

Pyrolysis of oil shale produces from 70 to 14,400 standard cubic feet of gas per ton of shale processed. The proper use and disposal of this low-Btu gas represents a significant challenge to the oil shale industry. The gas is highly corrosive, has low heating value and may contain high concentrations of such toxic trace elements as Hg, As, Se, and Cd. Lawrence Berkeley Laboratory is developing real-time instrumentation to measure toxic trace elements in oil shale gases and is using this instrumentation to measure As, Se, Cd, Hg, and Pb in gases from laboratory, pilot, and field retorts. A Zeeman atomic absorption spectrometer capable of making real-time, in-place measurements has been developed and used to demonstrate that Hg emissions from in-situ retorts may be nonuniform and that the majority of the Hg released occurs as a pulse towards the end of a run.

Oil shale processing may also produce from 0.1 to 22 barrels of water per barrel of oil. This water, which is highly contaminated, represents a potential resource for the arid oil shale region if it can be upgraded. Lawrence Berkeley Laboratory is exploring the use of various physical, chemical and biological processes to upgrade this water for in-plant use or discharge. This research has led to the development of a novel technique, termed spent shale adsorption, to reduce inorganic and organic carbon, color and odor of these waters.

Leachates produced by the interaction of rain or groundwater with spent residuals may degrade local water resources. Since the richer oil shale deposits are laced with groundwater, in-situ processing may result in significant underground contamination. Lawrence Berkeley Laboratory is investigating in-situ leaching and chemical transport in laboratory studies and by computer modeling and is searching for solutions to mitigate this phenomenon. This work has led to the identification of several possible control strategies and the development of a grout from spent residuals which may be used to seal underground retorts.

This report, which summarizes progress on these and other oil shale programs for the calendar year ending December 31, 1978, is an excerpt from the Energy & Environment Division Annual Report, 1978 (LBL-8619).

# Oil Shale Research

## Strategies for the Abandonment of In Situ Oil Shale Retorts

*P. Persoff, J. P. Fox, and P. K. Mehta*

INTRODUCTION

Oil is produced from oil shale by the pyrolysis of kerogen at 500 C or higher in surface retorts or in situ. Porosity is introduced into the formation by fracturing (true in situ) or by mining 20-30% of the shale followed by explosive fracturing of the remainder (modified in situ). Mined oil shale from modified in-situ (MIS) retorts may be stockpiled or processed in surface retorts. In-situ retorting leaves behind large underground retorts of spent shale separated by pillars of raw shale and surface piles of raw or spent shale (MIS retorting).

In situ processing may result in a number of environmental problems including degradation of local surface and ground waters, low resource recovery, and subsidence. The target of present oil shale commercialization activities is the Mahogany zone in Colorado's Piceance Basin. The oil shale resource in this area is sandwiched between two confined aquifers. During mining and retorting, these aquifers are dewatered. When the site is abandoned, groundwater will reinvade the area and flow through the abandoned retorts, leaching potentially toxic or carcinogenic materials from the spent oil shale. This material may then be transported in local aquifers, withdrawn in wells, or discharged into the Colorado River system as base flow. This is shown schematically in Fig. 1.

The structural integrity of in situ oil shale retorts is presently a concern. Oil shale loses considerable strength during retorting. This has resulted in one collapse during retorting. The long term structural stability of the retorts is uncertain and inadequate pillar strength and spent retort porosity may result in retort creep and subsidence in the long term. Low resource recoveries have been experienced with the in situ process. This is due to technical problems with rubblization, and to the necessity to leave about 25% of the resource in place as pillars to provide structural strength.

The objective of this project is to develop techniques to prevent or mitigate the potential environmental effects described above. Many conventional techniques, such as grouting, may not be feasible because of the large volumes and high costs involved. Therefore, the focus of this program is on developing new technologies that exploit on-site waste products and oil shale chemistry.

This program is funded by DOE's Division of Environmental Control Technology and was started in June 1978.

ACCOMPLISHMENTS DURING 1978

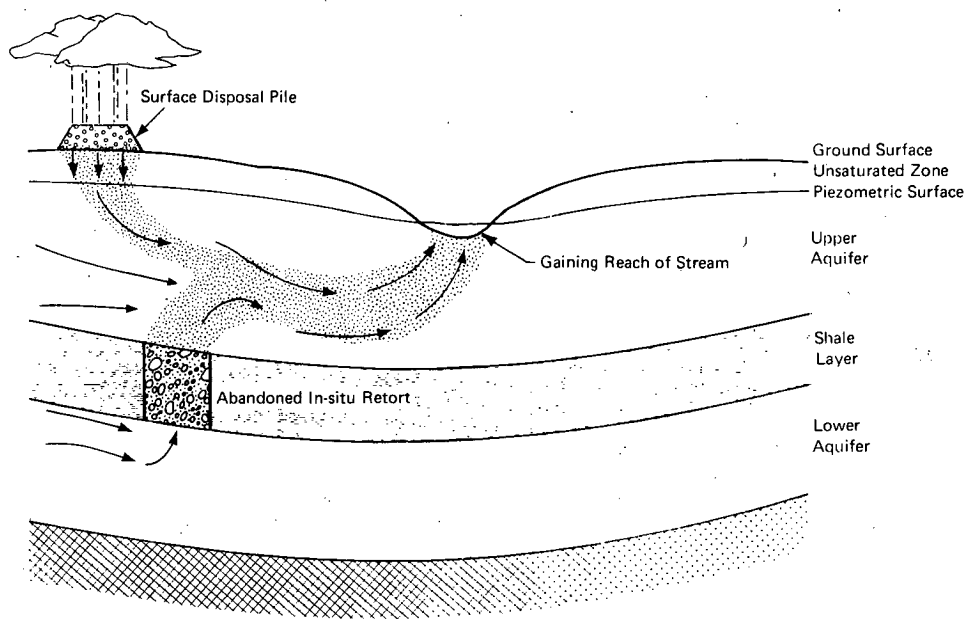A detailed assessment of environmental problems associated with in situ retorting and a literature



Fig. 1. Flow of leachates into gaining reach of a stream.
(XBL 791-178)

1

review on conventional control technologies used for related problems in other industries were completed. Preliminary estimates were made of the composition of leachate from in situ retorts and its probable dispersion and transport though local aquifers. These analyses indicated that it may take several centuries before significant degradation of local water resources occurs.

A variety of techniques has been used for flow blockage and strength development in underground formations in deep coal mining, oil field reservoir engineering, construction, and gas storage. An intensive literature survey was completed of the practices in these other industries and the resulting information interpreted in light of the unique problems facing in situ oil shale retorting. Conventionally, strength development and flow blockage are achieved by introducing a material called a grout into the formation. Materials used in these applications include portland cement, plastering agents, clays, emulsions, resins, gels, foams, and polymers. Preliminary cost estimates indicate that it could cost well in excess of several dollars per barrel of oil to apply these techniques to oil shale due both to the large quantity of material required to fill an in situ retort and to some rather unique problems in grout placement.

Cost analyses indicated that the only economically feasible solution would be one in which material costs were very low. This limited the range of possible solutions to those using on-site waste products or to novel approaches that do not require materials or difficult placement techniques. Possible solutions which have been identified include development of a hydraulic lime-pozzolan using surface retorted spent shale; placement of adsorbents; such as bentonite, into the abandoned retort; or formation of a CaCO$_3$ plug in situ using gas produced during retorting.

Production of a pozzolan from on-site waste materials is the most attractive option because it would simultaneously prevent surface and ground water disruption and provide for the disposal of surface spent shale. If sufficient strength could be developed, it might be possible to design retorts so that the pillars could be retorted, thus improving resource recovery. This technique is based upon the chemical similarity of spent shale and natural pozzolans which are siliceous and aluminous materials which combine with lime at ordinary temperatures to produce cohesive calcium silicate hydrates. Since spent shale has a substantial Ca content, true cementitious properties may be developed in spent shale by control of surface retorting conditions. A laboratory program has been initiated to determine the optimum cementitious properties that may be produced in spent shale. A summary of the proposed strategy under study is presented in Fig. 2.
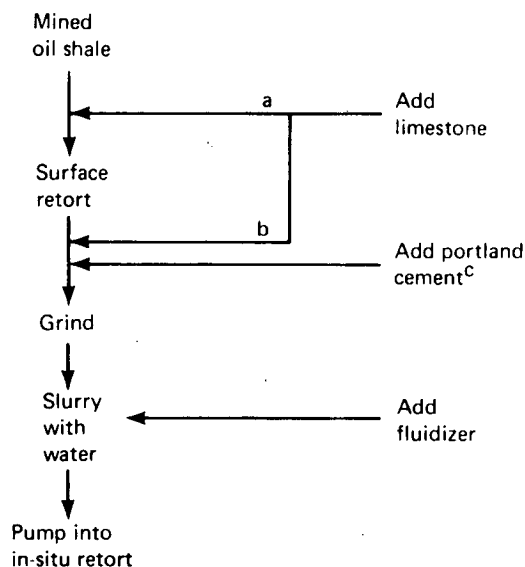


a. Add limestone before retorting if retorting temperature is high enough to calcine limestone.

b. Add calcined limestone after retorting if retorting temperature is not high enough to calcine limestone.

c. Portland cement addition only if strength development without it is inadequate.

Source: ref. 1

Fig. 2. Strategy for formation of a hydraulic lime-pozzolan from spent shale and its use for retort plugging.          (XBL 791-248)

PLANNED ACTIVITIES FOR 1979

Laboratory studies will be conducted to determine how grouts may be prepared from available on site waste products. The production of a hydraulic lime-pozzolan and formulation of a CaCO$_3$ precipitate in situ will be studied. Grout distribution through a thousand feet of overburden in an area that includes fractures, fissures, large voids and micropores will be studied.

REFERENCE

1. J. P. Fox, P. Persoff, M. M. Moody and C. J. Sisemore, "A strategy for the abandonment of modified in-situ oil shale retorts," Proceedings of the Environmental Symposium, November 28-30, 1978.

# Leaching of Organics from In Situ Spent Shale

*W. G. Hall, R. E. Selleck, and J. F. Thomas*

## INTRODUCTION

In many areas of the oil shale region, particularly in the Piceance Basin in Colorado, groundwater aquifers surround oil shale deposits that are being considered for commercial development. During in situ retort preparation and retorting, groundwater levels adjacent to the development site will be lowered below the retorts by pumping. After oil recovery is complete, the returning groundwater may pass through the spent oil shale rubble and leach out organic and inorganic compounds. Some of these may be toxic or carcinogenic and may be transported through the aquifers to surface waters and wells.

The principal objective of this investigation is to develop reliable kinetic data for leaching of organic compounds from spent shale so that a predictive model of the in situ leaching process may be developed. This model will be used by the Oil Shale Research Group in the formulation and investigation of alternative schemes to mitigate the impact of the leachate from abandoned in situ retorts on the regional water resources. Total organic carbon (TOC) and total dissolved solids (TDS) are the principal parameters of interest, although specific organic and inorganic constituents present in the leachate will be identified. This program was initiated in June 1978 and is funded by the Department of Energy's Division of Environmental Control Technology.

A series of batch and continuous flow leaching experiments was completed in a previous LBL study by Amy and Thomas.[1] TOC and electrical conductivity (EC) were measured in leachates from four different in situ spent shales at various water temperatures, salinities and leaching times. A main conclusion was that the kinetics of leaching of TOC from the spent shale appear to follow the laws of mass transport in fixed bed reactors but that the TOC leaching isotherms were extremely non-linear.[2] This created difficulties in evaluating the magnitude of the external and internal liquid film transfer coefficients, and the rate limiting steps were not ascertained.

The approach of the present investigation is to pump tap water through tightly packed columns of spent shale of varying diameters and lengths (to accommodate three different sized particles). Approach velocities in the empty cross section are about 0.3 m per day. Samples of leachate are withdrawn from the columns at intermediate and terminal points and are analyzed for TOC and EC. Columns are operated continuously until the concentration of leached organics falls below the detection limit of the analyical method used. Estimates of the leachable organic isotherms will be obtained directly from the column studies.

These may be supplemented by batch studies as required.

Possible readsorption of leached organics in aquifer material will be investigated by placing columns containing crushed oil shale in series with the spent shale columns. The effects of high salt content on the leaching of organics will be evaluated by passing saline water through one of the smaller columns and then comparing the results with those obtained using tap water. The saline water will be dosed to simulate natural groundwater.

## ACCOMPLISHMENTS DURING 1978

Fifty-five hundred kgs of spent shale were obtained from the Laramie Energy Technology Center's (LETC) 10-ton simulated in situ retort. The retort had been charged with 26 gallon-per-ton oil shale mined at Anvil Points, Colorado and ranging in size from fines to 60 cm. The maximum temperature reached during the run was 1200 F; steam was injected with the combustion air at a volume ratio of 67% air to 33% steam. Six leaching columns, 30 cm in diameter and 3 meters long, were constructed of standard galvanized corrugated steel culvert. Three smaller plastic columns with diameters from 10 to 15 cm were also constructed. A typical column is shown in Fig. 1. The columns are operated in the upflow mode with water entering the chamber at the bottom and leaving at the top. Sample taps of Tygon tubing are located at 15 cm intervals along the column so that leachate samples can be taken. Tap water is pumped from a reservoir by a variable speed Sigma pump set to deliver up to 10 ml per minute.

Results from one 220 hour long leaching run are shown on Fig. 2. A 10 cm diameter column was packed with spent shale particles having sizes from 0.3 to 1.3 cm. The shale column was 85 cm long. At the start of the run the column was filled rapidly with water and samples were taken immediately from each of the sample taps. Additional samples were then taken at intervals of 8 hours to 2 days. Figure 2 shows that the TOC concentration rapidly drops from the starting level to that of the influent in the time that it takes to pass six pore volumes of water. This suggests that it may be feasible to collect the leachate, treat it, and reinject it.

## PLANNED ACTIVITIES FOR 1979

Additional column studies will be conducted to obtain data for development of a mathematical model of organic leaching. Two-media column studies will be conducted to study adsorption-desorption mechanisms during aquifer transport of the leachate. Detailed organic characterizations of the leachate will be performed using gas chromatography, mass spectrometry and high performance liquid chromatography.
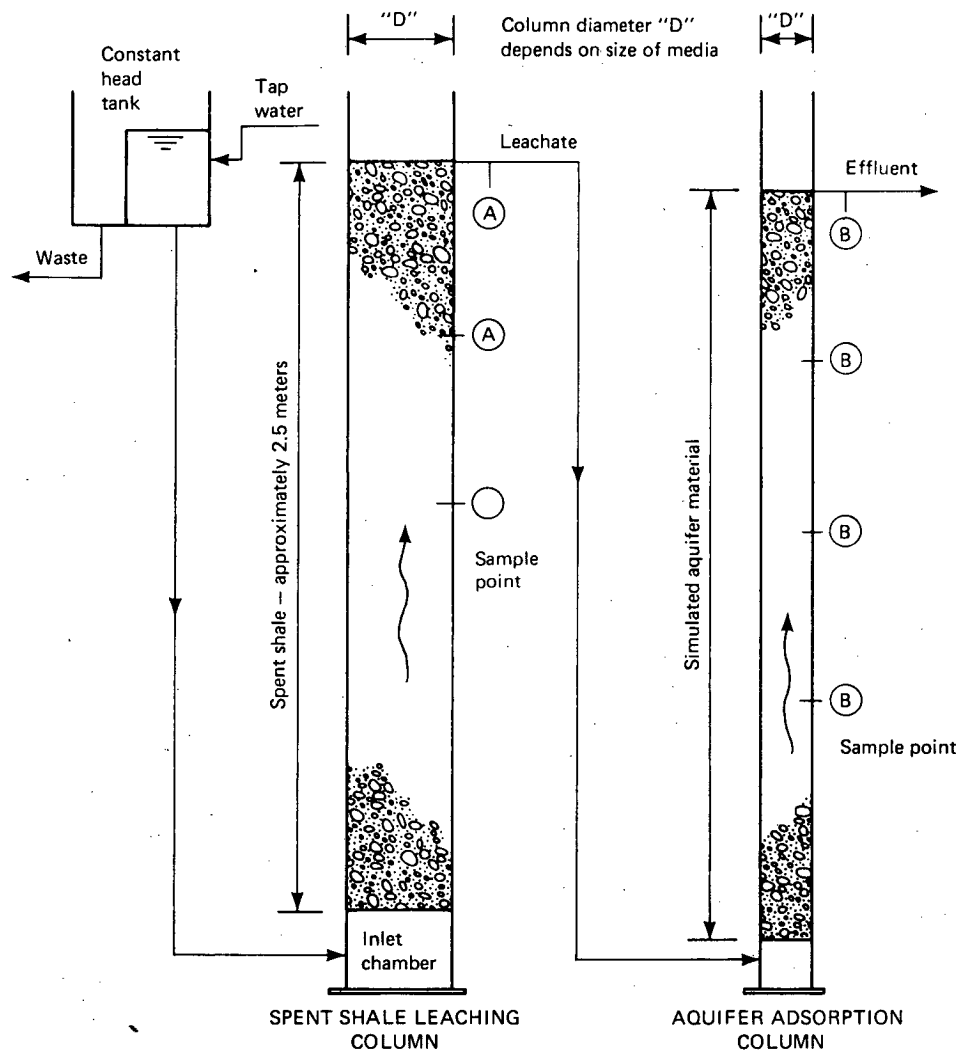
Fig. 1. Large column experimental set-up for organic leaching and adsorption.
(XBL 791-247)
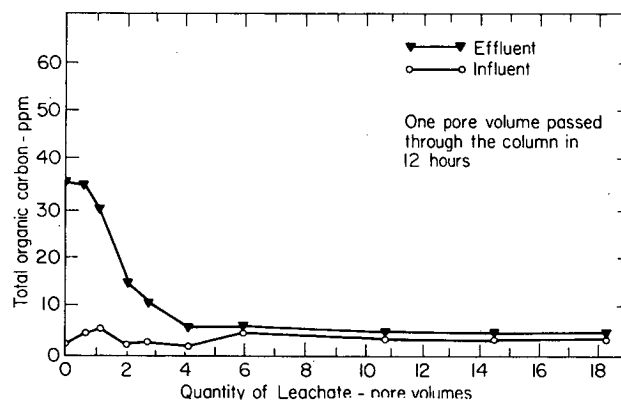


Fig. 2. Effluent levels of total organic carbon
in spent shale leachate.          (XBL 791-246)

REFERENCES

1. G. L. Amy and J. Thomas, "Factors that influence the leaching of organic material from in situ spent shale," Proceedings of the Second Pacific Area Chemical Engineering Congress, 1977.

2. G. L. Amy, "Contamination of groundwater by organic pollutants leached from in situ spent shale," Ph.D. dissertation, University of California, Berkeley, 1978.

# Geochemical Studies of an Oil Shale Deposit

B. Branstetter, R. D. Giauque, H. V. Michel, J. P. Fox,
R. B. Garrett, and L. Y. Goda

## INTRODUCTION

Oil shale is a marlstone that contains about 20% organic material. Green River oil shale was deposited from an ancient lake that covered parts of Colorado, Utah and Wyoming. This lake was probably permanently stratified. The upper portion may have supported an abundant microflora, and the lower layer was probably a sodium carbonate solution with a pH of 11 to 12. Oil shale was formed from constituents that entered this lake by overland runoff and atmospheric fallout of dust, pollen and volcanic ash. A complex series of geochemical processes produced the oil shale deposits that have appeared on the energy scene several times between 1850 and the present day.

The purpose of this program is to clarify the geochemistry of these deposits and develop information required to assess the deposits' commercial potential. The vertical variability of 45 major, minor and trace elements in the Green River Formation of Colorado is being determined by neutron activation analysis, x-ray fluorescence and other techniques. The results from these analyses will be used to assist in the evaluation of environmental impacts, environmental control strategies and to evaluate the recovery and utilization of some byproducts.

This program was initiated in June 1978 and is jointly funded by the Laramie Energy Technology Center (LETC), DOE's Division of Environmental Control Technology and Division of Fossil Fuel Extraction, the U.S. Navy, and the Environmental Protection Agency.

## ACCOMPLISHMENTS DURING 1978

Two cores from the Naval Oil Shale Reserve were sectioned and composited into 284 samples at 1, 2, 5, 25 or 50 feet intervals by LETC. The sample intervals selected were based upon presently known geologic stratigraphy and the type of technology likely to be used in commercial oil recovery (see Table 1). Sectioning of the cores was accomplished with a diamond saw. Each section was crushed and ground to 1/8 inch mesh particle size using a high-grade steel jaw crusher and a coffee-mill grinder. A standard splitting procedure was developed to randomly select representative 200 gram samples from composite samples weighing from 800 gm to more than 50 kg. Initially, analytical measurements were made on a number of sample splits to insure that the splitting procedure yielded representative, homogeneous samples. Analytical measurements were also made to insure that the samples were not contaminated by further grinding procedures preparatory to a complete analysis.

The analysis of the 296 samples is partially completed. Each sample is being analyzed for 45 major, minor and trace elements by several techniques yielding precisions of 0.1% to 5%. These include neutron activation analysis, x-ray fluorescence spectrometry, Zeeman atomic
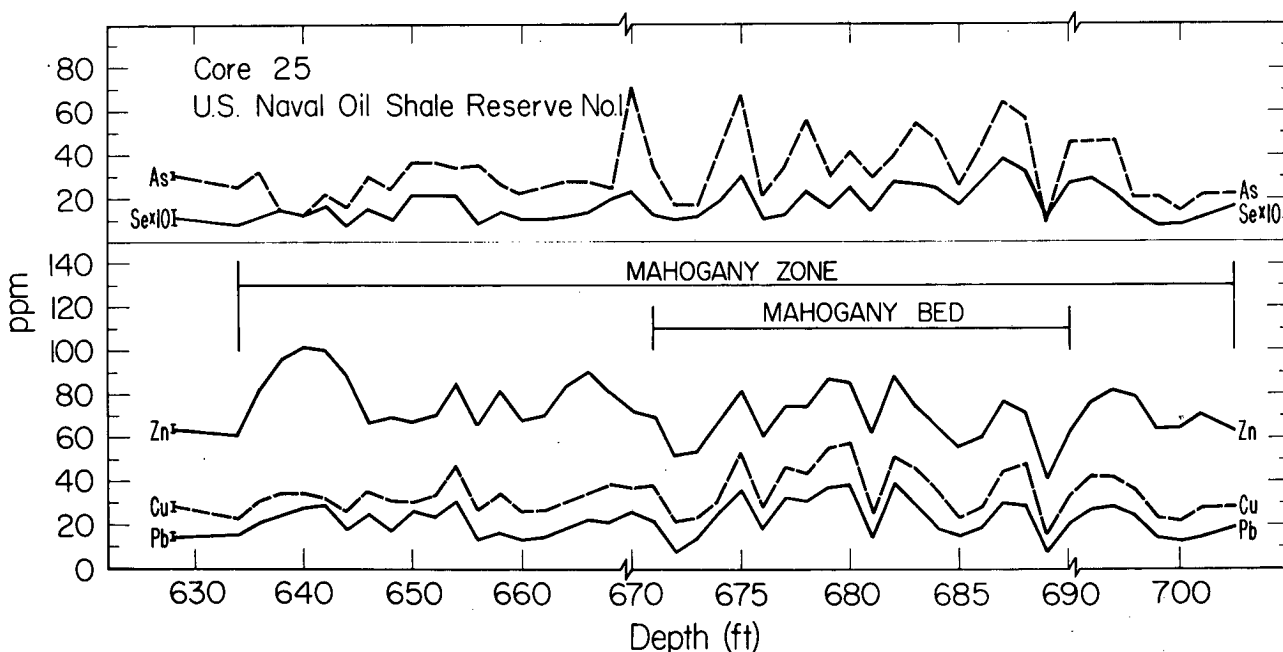


Fig. 1. Vertical variation in As, Se, Zn, Cu and Pb in the Mahogany Zone, Core 25, Naval Oil Shale Reserve No. 1. (XBL 7811-12689)

Table 1. Core stratigraphy and compositing plan

| Depth | Stratigraphy/ Technology | Feet of Core | Composite Interval In Feet | Number of Samples for Analysis |
|-------|--------------------------|--------------|----------------------------|-------------------------------|
| **Core Hole No. 15/16** | | | | |
| 856-1208 | Overlying oil shale; vertical modified retorting | 352 | 5 | 71 |
| 1244-1270 | Mahogany bed; mining with surface retorting | 26 | 1 | 25 |
| 1208-1346 | Mahogany zone; excludes Mahogany bed; vertical modified retorting | 138 | 2 | 57 |
| 1346-1372 | B Groove | 26 | 25 | 1 |
| 1372-1468 | Rich oil shale; vertical modified retorting | 96 | 5 | 18 |
| 1468-2019 | Poor oil shale; commercial development not anticipated | 551 | 50 | 11 |
| | TOTALS | 1163 | | 133 |
| **Core Hole No. 25** | | | | |
| 130-388 | Solution cavity zone | 258 | 50 | 5 |
| 388-634 | Overlying oil shale; vertical modified retorting | 246 | 5 | 49 |
| 634-705 | Mahogany zone; excludes Mahogany bed; vertical modified retorting | 50 | 2 | 25 |
| 670-690 | Mahogany bed; mining with surface retorting | 20 | 1 | 20 |
| 705-790 | Poor oil shales | 86 | 50 | 2 |
| | TOTALS | 660 | | 101 |

absorption spectroscopy, and plasma emission spectroscopy. Partial results from the analysis of one core are shown in Fig. 1. This figure shows the variation of As, Se, Pb, Cu and Zn in the Mahogany zone. The variation in these elements is similar to that observed for most other elements except U. This data and other similar results indicate that Cu, Pb, Zn, and Ni, which are typically associated with sulfide minerals, probably exist as carbonates in oil shales. This is consistent with the postulated geochemical origin of the lake. Other analyses suggest that the carbonate minerals act as diluent for other mineral phases.

PLANNED ACTIVITIES FOR 1979

Mineralogical studies including x-ray diffraction will be performed. Elemental analyses of the two cores will be completed. The resulting data will be statistically evaluated to identify vertical and lateral patterns and to clarify oil shale geochemistry.

# Partitioning of Major, Minor and Trace Elements During In Situ Oil Shale Retorting

*J. P. Fox, R. D. Giauque, A. L. Pacas, and J. F. Thomas*

INTRODUCTION

Oil shale, a marlstone with about 20% organic material, contains measurable quantities of many elements and significant quantities of such environmentally troublesome elements as U, Th, Zn, Cu, Pb, As, Se, Hg, Cd, F, B and others. These elements can reach the environment by direct discharge, by leaching, or during refining and use of the oil.

The purpose of this program is to study the partitioning of fifty-one elements during in situ oil shale retorting. Oil shale retorting produces shale oil, a low BTU gas, a solid waste referred to as spent shale, and an aqueous effluent known as retort water. Elements initially present in the oil shale are partitioned to these products during retorting. In this program, products from pilot-scale and field-scale retorts are collected and analyzed for major, minor and trace elements using neutron activation analysis, x-ray fluorescence spectrometry, Zeeman atomic absorption spectroscopy and other techniques. The effect of retort operating conditions and oil shale source, grade and particle size on elemental partitioning are being studied. Isothermal kinetic studies are conducted on the raw oil shale to identify reaction mechanisms. The resulting data are used to complete elemental mass balances and to investigate the effect of operating conditions, such as temperature and input gas composition, on the distribution of the elements. Environmental implications of observed trends are determined and control of partitioning by modification of retorting parameters is explored.

This program was initiated in 1976 and is funded by DOE's Division of Fossil Fuel Extraction. The program is a collaborative effort with the Laramie Energy Technology Center (LETC). The majority of the retorting experiments has been conducted at LETC and the analytical work, data reduction and supporting laboratory measurements at LBL. The program has focused on products produced by LETC's controlled-state retort and Lawrence Livermore Laboratory's (LLL) pilot-scale retorts. Previously, products were collected from a few runs of these retorts and used to develop suitable sampling and analytical methods and to identify the variables that control elemental partitioning. These methods were then applied to new retorting experiments to determine partitioning trends and responsible reaction mechanisms. The following section describes this work.

ACCOMPLISHMENTS DURING 1978

Products from 18 runs of the LETC controlled-state retort and 9 runs of the LLL retorts were collected and analyzed. The effect of

a range of conditions on partitioning trends was studied including temperatures from 500 to 1000 C; nitrogen, air and steam atmospheres; isothermal advance rates from 0.7 to 7.3 m/day; shale grades from 25 to 248 liters per tonne; and shales from Colorado, Utah, Michigan and Morocco. Typical elemental data for one of these runs are summarized in Table 1.

In addition to these completed runs, four interrupted runs of the LETC retort were studied. In an interrupted run, retorting is stopped midway by cooling the reactor with a water quench, and products are collected as a function of depth in the retort. Partial results from one interrupted experiment are summarized in Fig. 1. This figure shows the concentration of organic carbon, Hg, Cd and Fe as a function of depth in the retort. Organic carbon is typical of elements that are volatilized and removed from the retort as gas, oil and water (N, S, H). The organic carbon located 7 feet into the shale bed was volatilized and swept out of the retort. However, below 7 feet, the temperature was not high enough to volatilize the organic carbon. Hg and Cd concentrations indicate a sharp maximum just below the point
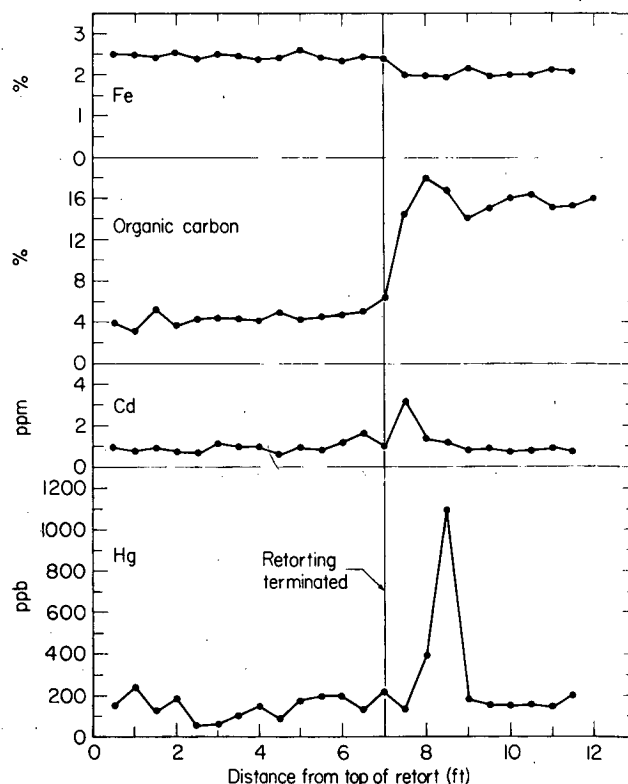


Fig. 1. The vertical distribution of Fe, organic C, Cd, and Hg in an interrupted run of LETC's controlled-state retort.     (XBL 791-238)

Table 1. Elemental abundances in products from a steam/combustion run of LETC's controlled state retort

| | Raw Oil Shale ppm | Spent Oil Shale ppm | Shale Oil ppm | Retort Water ppm |
|---|---|---|---|---|
| Al | 3.54 ± 0.06* | 4.18 ± 0.08* | < 0.4 | - |
| As | 44.7 ± 1.8 | 52.5 ± 2.1 | 7.92 ± 0.40 | 9.36 ± 0.48 |
| Ba | 488 ± 14 | 580 ± 13 | - | 0.57 ± 0.07 |
| Organic C | 14.8 ± 0.1* | 4.23 ± 0.01* | 84.1 ± 0.1* | 1.02 ± 0.01 |
| Inorganic C | 4.86 ± 0.01* | 4.33 ± 0.01* | - | 0.64 ± 0.01* |
| Ca | 11.0 ± 0.1* | 12.7 ± 0.1* | - | 23.8 ± 1.2 |
| Cd | 0.82 ± 0.20 | 0.74 ± 0.05 | < 0.014 | 0.0011 ± 0.0006 |
| Ce | 35.8 ± 0.6 | 48.6 ± 0.7 | 0.027 ± 0.005 | 0.0092 ± 0.0032 |
| Cl | < 0.15* | < 0.15* | - | 308 ± 4 |
| Co | 8.90 ± 0.17 | 11.7 ± 0.2 | 2.60 ± 0.02 | 0.469 ± 0.004 |
| Cr | 33.0 ± 0.6 | 39.6 ± 0.7 | 0.36 ± 0.02 | 0.31 ± 0.20 |
| Cs | 4.00 ± 0.12 | 6.51 ± 0.16 | - | 0.043 ± 0.001 |
| Cu | 33.8 ± 2.6 | 46.0 ± 3.0 | 0.52 ± 0.48 | < 0.09 |
| Dy | 2.00 ± 0.08 | 2.76 ± 0.09 | - | - |
| Eu | 0.554 ± 0.009 | 0.723 ± 0.010 | - | < 0.0001 |
| Fe | 1.90 ± 0.01* | 2.36 ± 0.02* | 63.2 ± 3.1 | 4.36 ± 0.22 |
| Ga | 7.8 ± 1.2 | 9.8 ± 1.4 | < 0.48 | 0.05 ± 0.04 |
| Ge | 1.2 ± 1.0 | 2.2 ± 1.2 | < 0.45 | < 0.06 |
| H | 2.07 ± 0.01* | 0.27 ± 0.02* | 12.2 ± 0.1* | - |
| Hf | 1.41 ± 0.05 | 1.99 ± 0.05 | - | 0.0049 ± 0.0003 |
| Hg | 0.062 ± 0.005 | 0.0095 ± 0.0021 | 0.029 ± 0.010 | 0.098 ± 0.005 |
| K | 1.38 ± 0.02 | 1.70 ± 0.02 | - | 36.1 ± 2.9 |
| La | 18.6 ± 0.5 | 24.7 ± 0.8 | 0.040 ± 0.003 | - |
| Lu | 0.146 ± 0.014 | 0.170 ± 0.015 | - | - |
| Mg | 3.5 ± 0.1* | 4.4 ± 0.1* | 29.2 ± 2.0 | < 27 |
| Mn | 287 ± 6 | 360 ± 7 | 0.354 ± 0.003 | 0.019 ± 0.012 |
| Mo | 25.6 ± 2.1 | 31.0 ± 2.5 | 0.59 ± 0.12 | 0.65 ± 0.02 |
| N | 0.64 ± 0.01* | 0.25 ± 0.03* | 1.94 ± 0.01* | 1.50 ± 0.01* |
| Na | 1.69 ± 0.05* | 2.26 ± 0.02* | 124 ± 1 | 1283 ± 10 |
| Nd | 16 ± 1 | 18 ± 2 | - | - |
| Ni | 20.1 ± 3.4 | 26.4 ± 4.0 | 6.85 ± 0.68 | 6.95 ± 0.92 |
| P | < 0.06* | < 0.06* | - | - |
| Pb | 21.3 ± 1.8 | 29.3 ± 2.0 | < 1.5 | 1.9 ± 1.2 |
| Rb | 57.2 ± 2.3 | 74.1 ± 3.0 | < 0.69 | 1.1 ± 0.5 |
| S | 0.56 ± 0.01* | 0.36 ± 0.01* | 0.65 ± 0.01* | 0.15 ± 0.01* |
| Sb | 2.01 ± 0.14 | 2.68 ± 0.17 | 0.022 ± 0.002 | 0.158 ± 0.001 |
| Sc | 5.55 ± 0.15 | 6.71 ± 0.18 | 0.0019 ± 0.0002 | 0.0043 ± 0.0090 |
| Se | 1.6 ± 0.6 | 2.4 ± 0.6 | 0.93 ± 0.01 | 0.385 ± 0.004 |
| Si | 13.1 ± 0.1* | 17.1 ± 0.1* | < 95 | - |
| Sm | 2.63 ± 0.13 | 3.47 ± 0.17 | 0.0020 ± 0.0005 | - |
| Sr | 733 ± 29 | 863 ± 34 | - | 0.21 ± 0.08 |
| Ta | 0.394 ± 0.004 | 0.513 ± 0.004 | - | - |
| Tb | 0.319 ± 0.088 | 0.396 ± 0.110 | - | - |
| Th | 6.01 ± 0.05 | 7.47 ± 0.06 | < 1.3 | 0.0094 ± 0.0004 |
| Ti | 0.12 ± 0.02* | 0.15 ± 0.01* | < 8.5 | < 20 |
| U | 4.47 ± 0.04 | 5.63 ± 0.05 | < 2.3 | 0.082 ± 0.001 |
| V | 118 ± 16 | 132 ± 15 | < 5.2 | 0.40 ± 0.28 |
| W | 2.2 ± 0.6 | 2.6 ± 0.6 | - | - |
| Y | 8.7 ± 1.0 | 14.9 ± 1.0 | < 0.99 | < 0.15 |
| Yb | 1.21 ± 0.03 | 1.56 ± 0.03 | - | 0.0021 ± 0.0004 |
| Zn | 59.4 ± 2.4 | 80.9 ± 3.2 | 0.53 ± 0.13 | 0.63 ± 0.06 |

* Weight percent

8

RETORTING PROCESS

Combustion zone
Pyrolysis zone
Reaction zone

Cool zone

Packed bed of oil shale

PARTITIONING MECHANISMS

REACTION ZONE

Oxide formation

*Sulfide*

$$MS \xrightarrow{\Delta} M \xrightarrow{O_2}$$
$$MS \xrightarrow{O_2} M_xO_y \longrightarrow xM + yO(g) \qquad (1)$$

*Carbonate*

$$MCO_3 \xrightarrow{\Delta} MO + CO_2 \qquad (2)$$

$$MO \xrightarrow{\Delta} M(g) + 1/2\, O_2(g) \qquad (3)$$

Reduction

*Carbon*
$$M_xO_y + yC \longrightarrow xM(g) + yCO(g) \qquad (4)$$

*Carbon monoxide*
$$M_xO_y + CO \longrightarrow xM(g) + CO_2 \qquad (5)$$

*Hydrogen*
$$M_xO_y + H_2 \longrightarrow xM(g) + H_2O \qquad (6)$$

COOL ZONE

Condensation

$$M(g) \rightleftharpoons M(s) \qquad (7)$$

Dissolution

$$M(\ell) \rightleftharpoons M(g) \qquad (8)$$

Solubilization

$$M_xO_y + H_2O \longrightarrow xM + OH \qquad (9)$$
$$MCO_3 + H_2O \longrightarrow M + CO_3 \qquad (10)$$
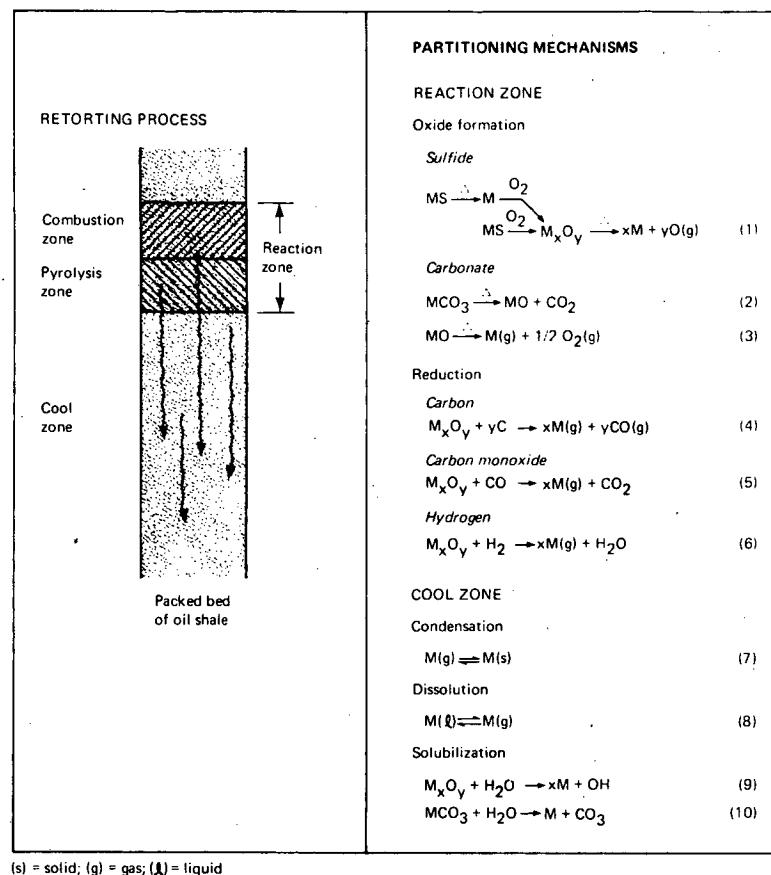
(s) = solid; (g) = gas; (ℓ) = liquid

Fig. 2. Summary of mechanisms that control elemental partitioning during in-situ oil shale retorting.　(XBL 791-239)

at which retorting stopped. This is due to condensation of these elements in cool regions ahead of the reaction front. Fe concentration variations are typical of elements that are not volatilized from the oil shale (Ca, Mg, Na, Cu, Dy, Al). Above 7 feet, the Fe concentration is higher since approximately 20% of the original oil shale has been volatilized.

The data from these experiments have been analyzed and interpreted to determine reaction mechanisms that control partitioning patterns and to identify environmental implications. These studies have indicated that most elements in oil shale are not volatilized and therefore are present in the spent shale. This is in sharp contrast to coal technologies where many more elements are distributed among the byproducts because of the higher temperatures reached in coal combustion or conversion processes. The only elements that are distributed in significant amounts (>1 wt. %) from the oil shale to the water, gas and oil are Cd, Hg, As, Se, Ni, Co, S, N, H, C and the halogens.

This study has revealed that the principal factors controlling elemental partitioning are mineralogical residence, retorting temperature and atmosphere, residence time of the oil within the reactor, product collection system design, and contact time between the oil and water.

Elemental partitioning is controlled by chemical reactions in the reaction zone and in the cool zone ahead of the reaction zone. These reactions are summarized in Fig. 2. In the reaction zone, which consists of a combustion zone followed by a pyrolysis zone, the oil shale minerals are decomposed and oxides are formed (Eqs. 1-3). Some metal oxides are then reduced by carbon, CO and hydrogen in the pyrolysis zone (Eqs. 4-6). The resulting volatile metal species are swept ahead of the reaction front by the input gas and are either condensed in cool regions ahead of this front (Eq. 7), are adsorbed by oil mist, swept out of the retort, or are dissolved in the oil/water emulsion (Eq. 8). The water that condenses out of the gas stream in cool regions ahead of the reaction zone leaches some constituents from the unreacted shale in the cool regions (Eqs. 9-10).

PLANNED ACTIVITES FOR 1979

Reaction mechanisms postulated to control elemental partitioning will be studied in laboratory isothermal kinetic programs. A field program will be initiated to test the applicability of laboratory studies to large-scale experiments.

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# Mobilization of Volatile Trace Elements During
# In Situ Oil Shale Retorting

## A. T. Hodgson and D. C. Girvin

## INTRODUCTION

### Background

The most economically attractive method
for the production of large volumes of oil
from oil bearing shales is in-situ retorting
whereby the shale is pyrolytically decomposed
in its original geological setting. First,
porosity is created in the shale bed; then
heat for pyrolysis is supplied by combustion.
The pyrolysis zone is driven down the shale
bed in front of the advancing combustion zone
by an introduced gas. The oil, water, and
gases formed during the process also move down
the bed, leaving behind a solid residue termed
spent shale. In-situ retorting of one ton
of moderately high grade shale would produce
25-30 gallons of oil, 10-660 gallons of water,
and 70-14,000 SCF of gas.

Department of Energy commercialization goals
call for the production of 100,000-250,000
barrels per day of shale oil by 1985. In order
to achieve the lower limit of desired production,
175,000 tons per day of oil shale would have
to be combusted. Processing of this quantity
of shale could produce as much as 116 million
gallons per day of retort water and two billion
SCF per day of gas. These large volumes of waste
materials are the focal point of environmental
issues associated with the use of oil shale.
The development of large-scale facilities to
reduce toxic constituents to acceptable levels
before the water and gas are released to the
environment presents a major technological
challenge.

### Project Objectives

In October of this year, our group initiated
a U.S. Environmental Protection Agency funded
research project to study the partitioning of
several toxic trace elements during simulated
in-situ oil shale retorting. This project
is specifically designed to determine how the
potentially volatile elements As, Cd, Hg, Pb,
Sb, and Se are distributed among the spent
shale, oil, retort water and offgas by the
retorting process. Emphasis will be placed
on making careful gas phase measurements of
these elements. A laboratory approach using
a bench-scale retort has been selected for
this investigation since field experiments are
considerably more expensive and are complicated
by contamination and sampling problems. The
operation of the laboratory retort during the
first and second years will allow us to develop
the instrumentation, analytical methodologies
and sampling strategies necessary for use in
third year experiments with several pilot-scale
retorts. In addition, the effects of retort
operating parameters on the distribution of
trace elements among oil shale products will be
determined under controlled laboratory conditions.

This information can then be used to predict
distributions for the field experiments. It
is anticipated that this program will provide
some of the information necessary to set emission
standards for As, Cd, Hg, Pb, Sb, and Se for
commercial in-situ oil shale processing plants.
Additionally, it will develop monitoring
strategies and analytical techniques suitable
for determining compliance with standards or
for making measurements at field installations
for the purpose of acquiring additional data
to set standards.

### Trace Element Mobilization

The way in which elements initially present
in raw oil shale are distributed among the
products during in-situ retorting is presumably
primarily controlled by retort operating conditions
and the mineral phases of the elements in the
starting material. The significant operating
conditions are thought to be maximum retorting
temperature, thermal advance rate, and input
gas composition and flow rate. Temperature
is a measure of the energy which controls
for chemical reactions including pyrolysis,
decomposition of carbonates and volatilization.
Thermal advance rate controls the residence
time of chemical species in the reaction zone.
Gas composition and flow rate govern the chemical
reactions that can occur at the gas-solid interface
and in the gas phase.

Mobilization of trace elements during retorting
is beginning to receive attention. Preliminary
investigations of pilot-scale plants indicate
that as much as 70% of the Hg present in raw
oil shale may be released in the offgas.
Comparable investigations have not yet been
conducted for As, Cd, Pb, Sb and Se; however,
limited mass balance data suggest that some
of the As, Cd and Se may also be released to
the atmosphere. No data are available for
Pb and Sb.

If 100,000 bbl/day production is realized,
uncontrolled emissions of volatilized trace
elements could have major environmental impacts
upon the lease tracts and surrounding areas.
For example, Hg, which is the most toxic and
volatile of the elements under investigation,
occurs in the raw oil shales of the Piceance
Basin, Colorado with an average concentration
of about 100 ppb. If 70% of this Hg is volati-
lized and released with the offgas, the result-
ing Hg emission would be approximately four
metric tons per year for a 100,000 barrel per
day industry. Baseline studies of the Colorado
lease tracts show that significant increases
would likely occur in the Hg concentrations
of the surface soils within one year if dispersal
over the tracts was uniform. However, dispersal
will almost certainly be non-uniform resulting
in areas of more rapid and intensive impact.

The elemental composition of retort waters from a number of pilot scale retorts has been investigated; however, the data are inconclusive since large variability resulting from analytical problems has been encountered. Nevertheless, As appears to occur consistently at concentrations greater than 1 ppm. In addition to concentration, the chemical speciation of trace elements in retort and receiving waters must also be considered. Retort waters contain high levels of carboxylic acids and organonitrogen compounds, which can bind trace elements in organic forms and thus affect their biological availability.

## ACCOMPLISHMENTS DURING 1978

The unique and innovative aspect of this program is the development of a continuous on-line monitoring technique for the elements of interest in gas streams containing high levels of organic compounds. The technique which we are employing is Zeeman atomic absorption (ZAA) spectroscopy which has been developed at LBL by Tetsuo Hadeshi. To date a ZAA instrument and furnace assembly for continuous Hg measurements has been constructed under a separate research contract described elsewhere in this Annual Report. Work is also continuing under a separate contract to develop stable light sources for As, Cd, Pb, Sb and Se. A laboratory scale, simulated in-situ retort has been designed and components are being evaluated. Development of analytical

methods to measure As, Cd, Pb, Sb and Se in oil and retort water samples has also been initiated. An ozonation cell equipped with an optional UV light source has been constructed to oxidize organic compounds which may interfere with trace element analyses in retort waters. The efficacy of this technique and its advantages over conventional oxidants have previously been demonstrated.

## PLANNED ACTIVITIES FOR 1979

In 1979 we will complete the construction of the laboratory retorting apparatus and continue the development of analytical techniques for the measurement of As, Hg, Cd, Pb, Sb, and Se in gas, oil and retort water samples. Interlaboratory and multimethod comparisons will be used to validate the preferred techniques. In the case of the gas phase analyses, the comparison techniques will be conventional acidic or basic impinger trains and adsorption tubes, as well as innovative wet or dry chemical collection methods.

Experiments to determine the effect of temperature and input gas composition on trace element partitioning during retorting will also be initiated. In these experiments, retorting temperatures and input gas compositions will be varied to reflect present commercial options, while other variables such as shale grade, particle size and heating rate will be held constant.

# On-Line Measurement of Mercury in Oil Shale Offgass Using Zeeman Atomic Absorption Spectroscopy

*D. C. Girvin and T. Hadeishi*

## INTRODUCTION

Oil shale offgas is a complex and highly variable corrosive mixture containing significant quantities of entrained oil mist, hydrocarbons, $CO_2$, CO, $H_2S$ and $NH_3$. Preliminary investigations of simulated in-situ oil shale retorts suggest that significant concentrations of mercury (Hg) may be present in this gas and emitted to the atmosphere during commercial oil shale retorting.[1]

Major sampling and analytical problems have plagued previous investigators who have attempted to measure volatile trace elements in this gas with wet chemical collection devices, such as impinger trains, or with direct spectroscopic measurements. The purpose of this project is to determine the concentrations and fluxes of Hg in the product gases from several field experiments and to investigate the chemical mechanisms and physical processes controlling these fluxes. Zeeman atomic absorption spectroscopy will be developed to continuously analyze Hg and possibly other elements in these gas

streams. This program was initiated in August 1978 and is funded by the Environmental Protection Agency and DOE's Division of Environmental Control Technology.

Zeeman atomic absorption spectroscopy (ZAA) is a modification of conventional atomic absorption spectroscopy in which the light source is placed in a magnetic field. This splits the original resonance line into its linearly ($\pi$) and circularly ($\sigma$) polarized Zeeman components. The gas monitor being developed consists of four major components: a light source which provides a resonance emission line ($\pi$) and reference lines ($\sigma$) for background (smoke) correction; a furnace-absorption tube assembly where sample gas is thermally decomposed and swept into the light path of the detection and reference beams; a detector which converts changes in intensity of the transmitted detection and reference beams into an analog signal; and the signal processing electronics.

Prior to the initiation of this project in August, an existing Zeeman Atomic Absorption Spectrometer (ZAA), equipped with a R.F. source

and a furnace designed for batch analysis of liquids and solids, was used to make continuous on-line measurements of mercury in the product gas during an 80-hour burn of Laramie Energy Technology Center's (LETC) controlled-state retort.[1] This brief experiment demonstrated that ZAA can measure mercury and probably other elements in the presence of significant amounts of organics and smoke from incomplete combustion of entrained oil mist. This is due to the unique background correction ability of ZAA. It was also found that mercury concentrations in the gas stream vary by orders of magnitude during the retorting process. This variation is due to the successive volatilization and condensation of mercury as the retort reaction front propagates down the shale bed (Fig. 1). This kind of emission behavior can only be detected by continuous on-line analyses. No long-term direct gas measurements during field in-situ retorting experiments are available to corroborate these laboratory results. Verification of our LETC observations during a larger scale test is necessary so that control technology can be developed if necessary. This requires a significant improvement in instrumentation.

The primary objective during the first year of this project is to develop ZAA instrumentation capable of continuously measuring mercury concentrations in offgases on a real time basis under field and laboratory conditions. This will require modifications in the design of ZAA spectrometers. Light source and furnace assemblies must be redesigned to accommodate gas flows and severe field conditions. In addition, dynamic calibration methods and a gas sampling system capable of accurate metering and control of sample and calibration gases must be developed. Corrosion of the furnace due to sulfidation reactions will be investigated. When development and testing is completed, ZAA gas analyzers will be used to make long-term mercury measurements during laboratory and field retorting experiments.

ACCOMPLISHMENTS DURING 1978

A field ZAA spectrometer for on-line Hg analyses was designed and built during 1978.

This instrument incorporates some significant advances in state-of-the-art Zeeman atomic absorption spectroscopy and gas monitoring. These are discussed here.

Light Source

A new, low pressure, Hg, gaseous discharge lamp has been built and tested which will replace the R.F. excited electrodeless discharge (EDL) previously in use. This "pen light lamp" (PLL) consists of a U-shaped quartz tube containing argon and a small quantity of Hg. Minute electrodes are sealed in each end of the tube. The outer diameter of the tube is 7 mm. The lamp is surrounded by a soft iron water jacket fitted with a quartz window. The lamp-water jacket assembly fits between the pole tips of the permanent magnet which produces the Zeeman splitting of the resonant lines. The argon plasma and Hg resonance lines are produced by a 1 kHz high voltage driver. The 2357 Å line intensity obtained with the PLL is approximately 50 per cent greater than that obtained with the EDL.

A major problem with the old EDL was the variation of intensity of the 2357 Å line and the variation of instrumental baseline with changes in ambient temperature. This represented a serious problem for field application where significant temperature fluctuations are likely to occur. However with the PLL this problem has been eliminated by coupling the water jacket to a constant temperature bath. Another problem with the EDLs was the R.F. pickup in adjacent instruments (e.g., thermocouples, and flow transducers) due to the R.F. excitation of the argon plasma. This problem has also been eliminated by the use of the PLL. Overall, the Hg PLL offers a significant improvement in ZAA versatility and performance.

Gas Sampling System

The gas sampling system is shown in Fig. 2. Sample gas is pumped into a heated stainless steel sample tube. To prevent condensation of mercury on the walls, this tube is maintained
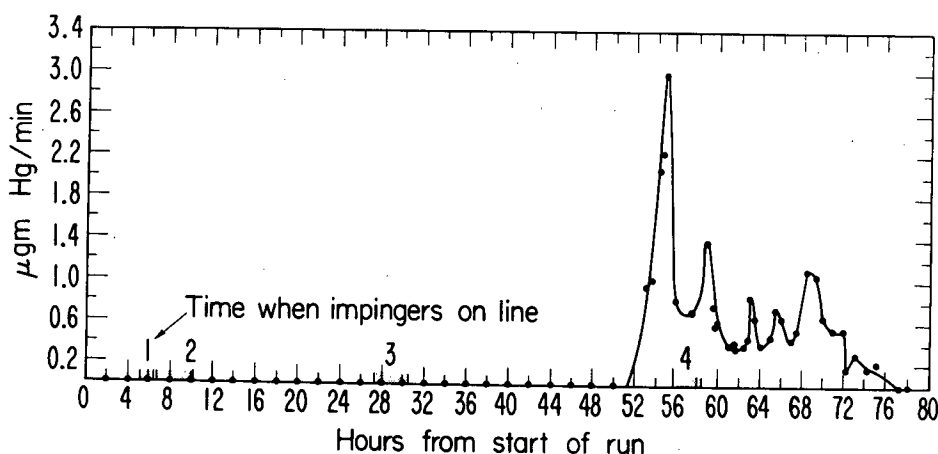


Fig. 1. The distribution of total mercury in the offgas of a steam/combustion run of LETC's controlled-state retort. (Ref. 1)                                             (XBL 784-711)
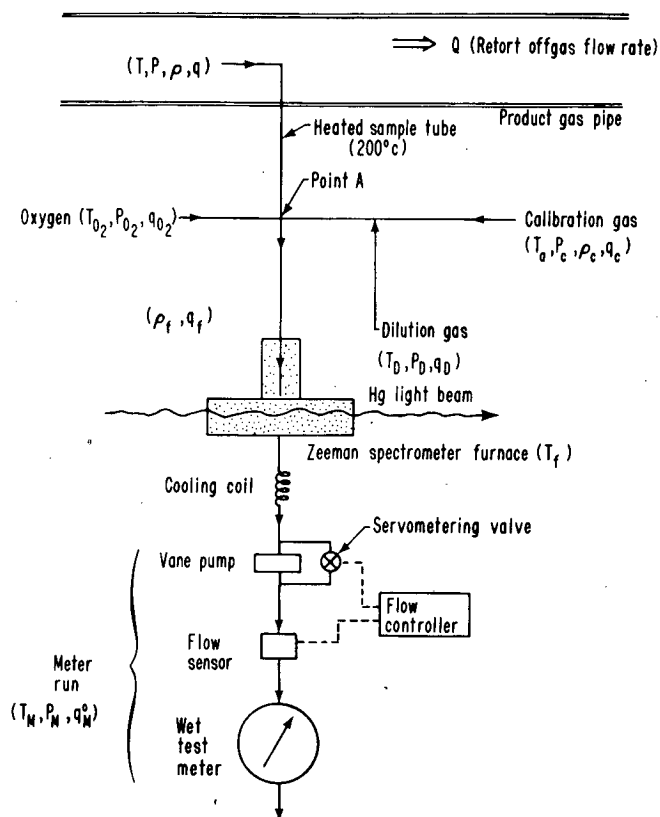
Fig. 2. Furnance assembly and gas sampling system of the Zeeman atomic absorption gas monitor. (XBL 792-480)

at approximatly 200°C by joule heating. Oxygen is continuously introduced into the sample line to promote combustion of organics and thus reduce the level of smoke in the ZAA furnace. Calibration is achieved by introducing a carrier gas saturated with mercury vapor. Dilution gas is also introduced to the sample line to extend the calibration range. These gases are mixed and are then pumped into the combustion chamber of the furnance where they are heated to 900°C to atomize the mercury. The density of mercury atoms in the absorption chamber of the furnace is then measured by the ZAA. The gas leaving the furnace is cooled to reduce corrosion in the downstream pump and flow controller. Furnace temperature and the volumetric flow rate of gas through the furnace (Q) must be held constant between calibration runs. ZAA furnace temperature are maintained to within ± 10°C. Q is measured and held constant (2% of reading) by a flow controller. The flow controller is calibrated with a wet test meter downstream of the controller.

## Furnace - Absorption Tube Assembly

Mercury and its compounds atomize (thermally decompose into individual atoms) below 900°C. To date we have succeeded in building a mercury

furnace capable of operating at 900°C for extended periods. The current design is shown in Fig. 2. Number 321 stainless steel tubing, 1/2 inch OD, is welded into a "T". The atomization chamber is filled with ceramic chips to break up the gas flow and increase the surface area for thermal contact. The adsorption and atomization chambers are separated by a narrow passage. Quartz windows pass the 253.7 nm resonance line of mercury while isolating the hot sample gas from the cooler ambient air. Temperatures of 900°C are attained in the atomization chamber by joule heating for gas flow rates as high as 10 ℓ/min. Temperatures in the absorption chamber are lower since the current in each leg is 1/2 of that flowing through the walls of the atomization chamber. Current is supplied to the furnace via thin strips of 304 stainless steel welded to the tubing. When the furnace is at its maximum temperature, the outer ends of these variable cross section strips are cool enough so that resistive oxide layers do not build up on power connector surfaces. In addition, these strips act as furnace mounts providing both the rigidity to maintain optical alignment and the flexibility necessary to accommodate expansion during heatup.

The presence of $H_2S$ in oil shale offgases creates a serious corrosion problem in the furnace. ($H_2S$ concentrations can exceed several molar percent.) Sulfidation reactions are the main cause of this problem. In an attempt to inhibit corrosion and maximize furnace lifetime the stainless steel furnaces have been alonized. Alonization is a process whereby alumina is diffused into the surface of the tubing and welds. Based upon the work of others studying corrosion of stainless steel in oil shale atmospheres, this protective coating of alumina should significantly increase the lifetime of ZAA furnaces.

## PLANNED ACTIVITIES FOR 1979

Corrosion tests will be conducted on alonized and untreated stainless steel furnance assemblies. The field mercury ZAA will be tested and used during laboratory retort experiments. Improvements resulting from these tests will be incorporated and the instrument will be used during at least one and perhaps several in-situ field experiments. The need for control technology to reduce mercury level will be assessed, based on these field measurements.

## REFERENCES

1. J. P. Fox, J. J. Duvall, K. K. Mason, R. D. McLaughlin, T. C. Bartke and R. E. Poulson, "Mercury emissions from a simulated in-situ oil shale retort," Proceedings of the Eleventh Oil Shale Symposium, Colorado School of Mines, Golden, CO, April, 1978.

# The Biological Treatment of Oil Shale Process Waters

*J. P. Fox, L. A. Tom, L. J. Tom, and D. E. Jackson*

## INTRODUCTION

Oil shale retorting produces from 0.10 to 22 barrels of water per barrel of oil. For a 500,000 barrel per day plant, which represents about 6% of the 1977 US crude oil production, this represents about 4 to 550 million gallons of water, depending on the type of process and plant location. This water, referred to as retort water, originates from combustion, mineral dehydration and groundwater. The waters are yellow to brown in color, have a pH that ranges from 8.1 to 9.4 and may contain high concentrations of $HCO_3$, $SO_4$, $S_2O_3$, $NH_4$, Na, and Cl and organic carbon. The organic constituents are primarily polar, and carboxylic acids comprise the principal group.

This water represents a potential resource for the arid areas in which oil shale is located if it can be upgraded. Work completed to date indicates that treatment of this water is particularly difficult due to the high levels and variety of constituents present. Any potential use of retort water will likely require the removal of some or all of the organic material. Work completed at other institutions indicates that conventional processes, including carbon adsorption, lime treatment, chemical oxidation, electrolytic oxidation and several aerobic biological processes are not suitable for the reduction of organics from retort waters.

The purpose of this study is to investigate the removal of soluble organics from retort water by anaerobic fermentation and activated sludge. The direct use of activated sludge to treat retort water is limited by oxygen transfer in the aeration tank (the BOD levels are very high) and by the presence of many toxicants. In this work, the use of anaerobic fermentation as a pretreatment step for activated sludge was investigated. Anaerobic fermentation is a two stage biochemical process. Organics in the waste are converted to carboxylic acids by a group of facultative and anaerobic bacteria referred to as the "acid formers". These acids are then converted into $CO_2$ and $CH_4$ by a group of anerobic bacteria referred to as "methane formers". This process is particularly suited to wastes with high concentrations of carboxylic acids, such as retort water, as the bioconversion of these constituents is rapid. The process not only stabilizes a larger fraction of the organic matter than other biological processes, it also has lower nutrient requirements, produces less sludge, and is adaptable to intermittent loadings.

This program was initiated in 1977 and is funded by the Laramie Energy Technology Center. Previously, several digesters were set up and used to treat retort water. This work indicated that retort water must be pretreated to remove toxic constituents and to supplement nutrients.

Additional work was conducted durinq this period to verify these experiments, to identify and isolate toxic components and to investigate the use of activated sludge to biodegrade the organics in the effluent from an anaerobic digester. The results of this phase of the program are described below.

## ACCOMPLISHMENTS DURING 1978

Four anaerobic digesters were acclimated and fed retort water from LETC's 150-ton retort and from a Geokinetics field experiment. The retort water was treated to remove oil and grease, suspended solids and ammonia, the pH was adjusted to 7, and the nutrients Ca, Mg and P were added. A schematic of the digesters used in these experiments is shown in Fig. 1. The composition of the 150-ton retort water is shown in Table 1. Daily measurements were made of the COD, TOC and volatile acids in the effluent and in the digester, and gas production and composition were determined. The result of one such experiment is shown in Fig. 2. This figure shows the effect of nutrient additions on the COD in the digester effluent. Prior to day 34, the volatile acids and COD levels in the effluent steadily increased suggesting that carboxylic acids produced by the "acid formers" were not being converted to methane. Both volatile acids and COD dropped to low levels after nutrient addition and remained there. Reductions in organic carbon obtained using this process ranged from 60 to 70% for hydraulic residence times of 30 to 50 days for the 150-ton retort water; the process failed when Geokinetic retort water was used. These long hydraulic residence times are not typical of anaerobic fermentation and limit the practical utility of the process for the treatment of large volumes of retort water.

It was postulated that the long residence times were due to an inhibitory effect of a constituent present in the retort water. Powdered activated carbon, which is an excellent adsorbent, was added to one digester. This did not improve the performance of the digester. The effect of SCN present in the retort water (525 mg/$\ell$) was investigated by dosing a control digester with artificial substrate spiked with SCN. Measurements of SCN in the influent, the digester and the effluent indicated that there was no conversion of SCN during anaerobic fermentation and that SCN was not toxic at levels present in retort water.

A series of experiments was conducted using the extended aeration activated sludge unit shown in Fig. 3. The effluent from one of the digesters was introduced into the activated sludge unit. This unit reduced the organic carbon by about 80%, which is considered excellent. In other experiments, the pretreated retort water was introduced directly into the activated
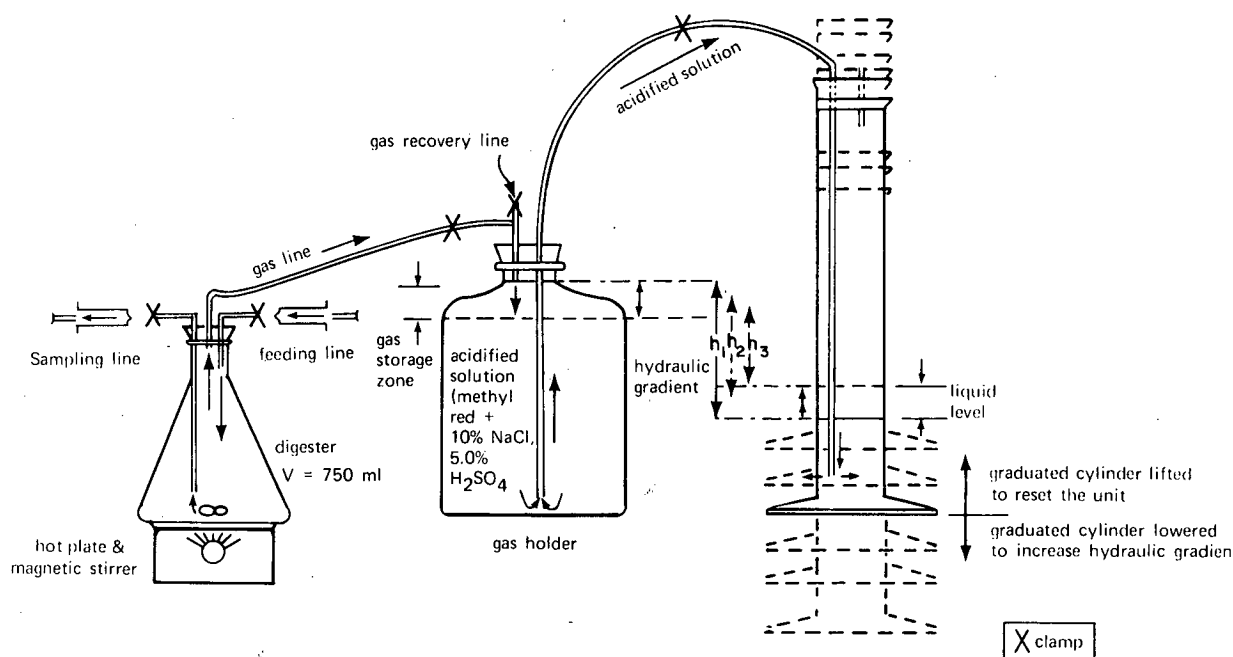
Fig. 1. Schematic of anaerobic acclimation system. (a) Digester's contents are mixed and kept at constant temperature (35 ± 1°C) by means of a hotplate-magnetic stirrer. (b) Fermented gas is introduced into a gas holder unit by means of a slight negative pressure created by the water column differential (h). The gas holder unit contains an acidified solution to prevent the dissolution of $CO_2$. The gas, on entering the gas holder, displaces some of the acidified solution which is collected in the graduated cylinder. This volumn of acidified solution is used to calculate the volumn of gas produced. (c) The fermentation gas is recovered and the acidified solution level reset by lifting the graduated cylinder and properly operating the valves. (XBL 7710-2163)

Table 1. Composition of retort water from a combustion run (Run 13) of LETC's 150-ton retort (mg/ℓ)

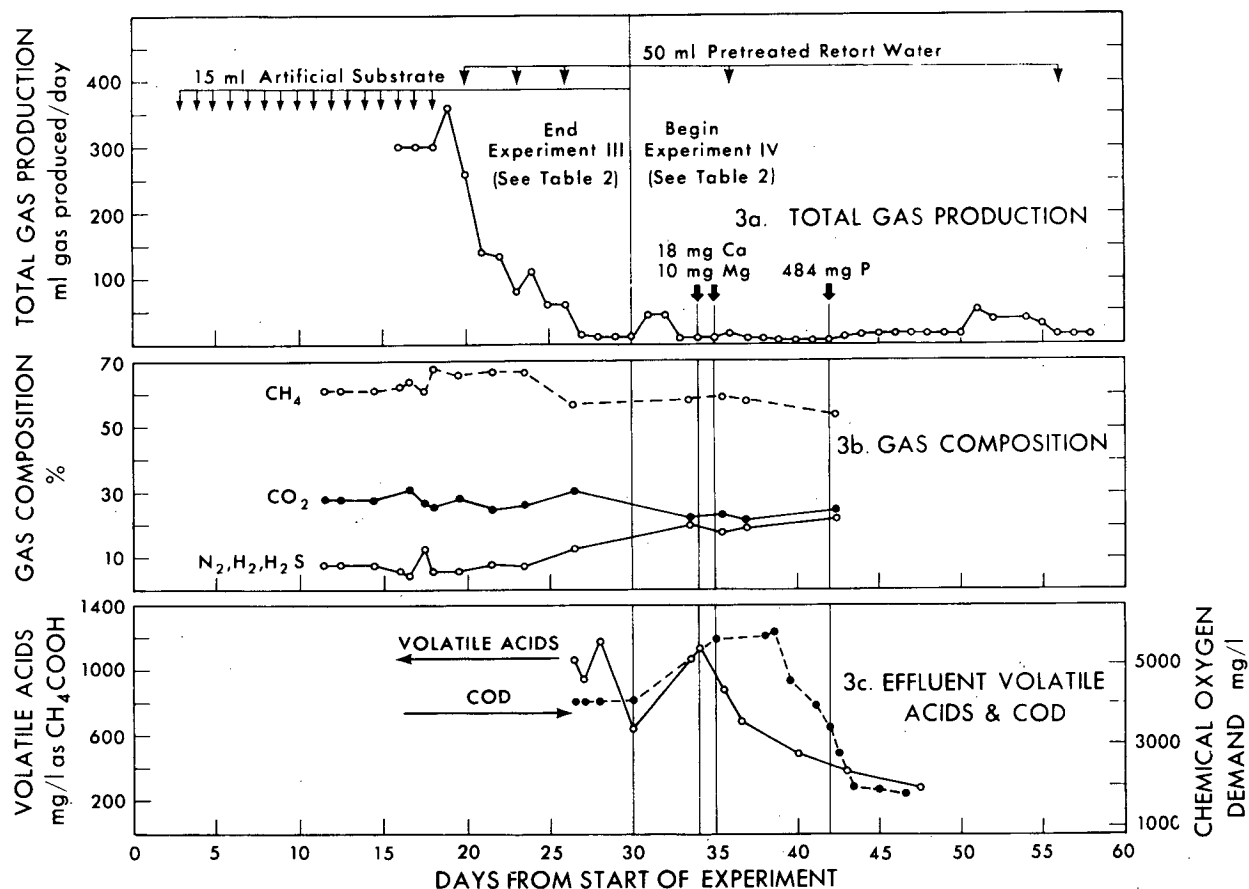| | Raw Retort Water | | Raw Retort Water |
|---|---|---|---|
| Akalinity, Total (mg/ℓ CaCO$_3$) | 38,000 | Magnesium | 24 |
| Aluminum | 16.6 | Manganese | 0.22 |
| Arsenic | 1.4 | Nickel | 0.014 |
| Barium | 0.17 | Nitrogen, Total NH$_3$ (as NH$_3$) | 10,150 |
| Biochemical Oxygen Demand, | | Nitrogen, Kjeldahl (as N) | 11,000 |
| 5-day (BOD$_5$) | 5,325 | pH | 8.6 |
| Boron | 3.4 | Phosphorus (as P) | 8.5 |
| Bromine | 1.5 | Potassium | 37 |
| Calcium | 3.3 | Selenium | 0.24 |
| Carbon, Inorganic | 5,850 | Silicon | 25 |
| Carbon, Total Organic (TOC) | 4,980 | Sodium | 655 |
| Chemical Oxygen Demand (COD) | 8,800 | Solids, Total Dissolved | 4,210 |
| Chlorine | 57 | Solids, Total | – |
| Chromium | 0.018 | Solids, Volatile | – |
| Cobalt | 0.31 | Solids, Suspended | – |
| Copper | 15.6 | Sulfate (as SO$_4$) | 1,100 |
| Fluorine | 26 | Sulfur, Total (as S) | 406 |
| Hardness (as CaCO$_3$) | 86 | Vanadium | 1.8 |
| Iodine | 0.11 | Volatile Acids (as CH$_3$COOH) | 3,300 |
| Iron | 4.7 | Zinc | 6.4 |
| Lead | 0.3 | | |

Fig. 2. Time variation of total gas production, gas composition, volatile acids and chemical oxygen demand. (XBL 7710-2162)
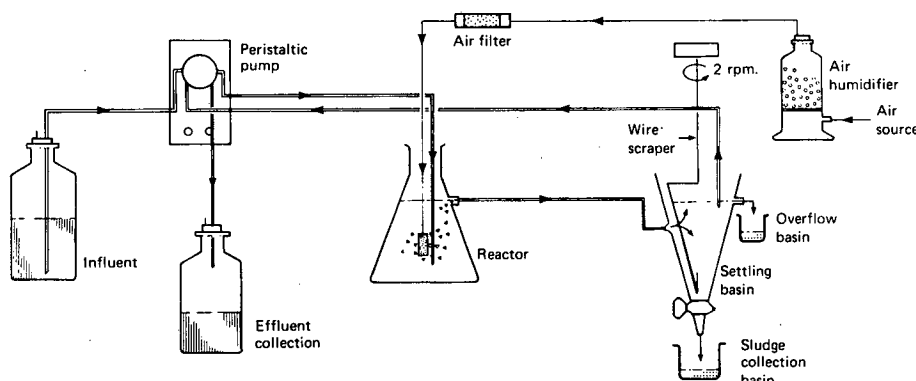


Fig. 3. Schematic of extended aeration activated sludge system. (XBL 791-243)

sludge unit. This resulted in organic carbon reduction of about 30% which, again, indicates an inhibitory effect. Although good organic reductions were obtained by using anaerobic fermentation and activated sludge in series, the sequence is limited by the high hydraulic residence time of the digester, and therefore could not be effectively used in a large-scale treatment facility.

This study, to date, has indicated that biological treatment of retort water may be viable if the inhibitory and toxic effects of yet unidentified constituents can be resolved. This may be overcome by either

identifying the troublesome components and determining methods to remove them, or by developing a strain of bacteria which is immune to these constituents.

PLANNED ACTIVITIES FOR 1979

Other research has indicated that some types of bacteria proliferate in containers of retort water maintained at room temperatures. During the next fiscal year, a program will be initiated to determine if these bacteria can be acclimated and used to remove a significant fraction of the organics in retort water on a large scale.

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# Spent Shale as an Adsorbent for Organics

*D. E. Jackson, R. N. Anaclerio, and J. P. Fox*

INTRODUCTION

Oil shale retorting produces 0.10-22 gallons of retort water and about 70 pounds of spent shale for each gallon of oil, depending on plant location and retorting conditions. The retort water, which contains high levels of many organic and inorganic constituents, would be a valuable resource for the arid regions in which oil shale deposits are located, provided that effective and economical treatment methods can be found.

The goals of this project are to determine whether retorted oil shale can be used as an adsorbent to remove organic constituents from oil shale processing wastewaters (retort water) and, if so, to use it in a treatment sequence that includes biological processes. This program was initiated in June 1978 and is funded by DOE's Division of Environmental Control Technology.

Past attempts to adapt conventional treatment technologies such as anaerobic fermentation, trickling filters, activated sludge, carbon adsorption, or oxidation to remove organics from retort waters indicate that these methods have serious technical or economic limitations. However, an observation made at LBL during the course of other work suggested another solution. A normally non-adsorbing dye, pontacyl pink, was passed through a packed bed of spent shale in order to study the flow of water through the column; the experiment failed because the dye was adsorbed on the shale. This observation, supported by subsequent adsorption studies done elsewhere[1], suggested that spent shale might be used in a treatment step to reduce the level of organic constituents in retort waters.

Raw oil shale contains a complex organic component called kerogen that is imbedded in a mineral matrix. The pyrolytic decomposition of kerogen that occurs during retorting removes most of the organic material, leaving behind a complex system of pores and cavities that we think will provide the large surface area that is required for effective adsorption. Calculations from an isotherm obtained for the sorption of $SO_2$ on one spent shale[2] show that it has a specific surface area of roughly $5 m^2/g$. Although this is more than two orders of magnitude lower than the specific surface area of activated carbon, we hope that the low cost and on-site availability of spent shale will compensate for its lower efficiency.

ACCOMPLISHMENTS DURING 1978

Since the project began in June 1978 we have completed the necessary preparatory work and have begun preliminary adsorption studies. We have collected samples of spent shales that have been retorted under various conditions and separated them by particle size, as well as collecting and storing a variety of retort waters generated at the Laramie Energy Technology Center and Lawrence Livermore Laboratory.

Much effort has been devoted to developing a combustion-IR method of determining the levels of organic carbon in these waters that is free of interference by the other constituents. Following the elimination of carbonate, the samples are combusted in an $O_2$ stream at 950°C, and the $CO_2$ in the gas stream is determined with a non-dispersive IR spectrophotometer. The waters have been characterized, and their homogeneity and stability during storage have been investigated.

A few preliminary batch studies to determine the adsorptive capacity of the shales have been completed. The results of one of these experiments are summarized in Table 1. The batch studies were carried out on varying amounts of different spent shales and retort waters. The spent shale was weighed, placed in a 250 ml Erlenmeyer flask and then a measured amount of retort water was added. The flasks were sealed and placed on a mechanical shaker for varying amounts of time. Small samples were obtained by filtering a few milliliters of sample through a 0.45 m Millipore filter, and analyzed for pH, organic carbon, inorganic carbon and conductivity. These studies indicated

Table 1. Batch adsorption experiment in which 50 g of 150-ton spent shale and 50 ml 150-ton retort water are contacted for 144 hrs.

| | |
|---|---|
| Initial dissolved organic carbon, mg/ℓ | 3300 |
| Final dissolved organic carbon, mg/ℓ | 2510 |
| Percent reduction in dissolved organic carbon | 24% |
| Specific adsorption, mg organic carbon/g shale | 0.80 |
| Initial pH | 8.8 |
| Final pH | 10.1 |
| Initial conductivity, μmhos/cm | 36,000 |
| Final conductivity, μmhos/cm | 18,000 |
| Percent reduction in conductivity | 50% |
| Initial inorganic carbon, mg/ℓ | 6400 |
| Final inorganic carbon, mg/ℓ | 340 |
| Percent reduction in inorganic carbon | 95% |

that a 1:1 weight ratio between spent shale and retort water was necessary to observe measurable amounts of adsorption. Table 1 indicates that the dissolved organic carbon was reduced by 24%, the electrical conductivity by 50%, the inorganic carbon by 95% and the pH was elevated from 8.8 to 10.1 after contacting 150-ton water with 150-ton shale for 144 hours. The reduction in inorganic carbon is believed to be due to a process of exchange between carbonate in the water and hydroxide formed from the hydration of CaO or other metal oxides as follows:

$$Ca(OH)_2 + HCO_3^- \rightleftharpoons CaCO_3 + H_2O + OH^-$$
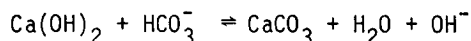
These results verify the assumption that spent shale will remove organics from retort water. The organic carbon reduction of 24% is not as large as we anticipated. A series of studies has been initiated to determine if the adsorptive properties can be improved by chemically or physically treating the shale. Methods under study include heat treatment, acid leaching and pH adjustment. However, this may not be a serious limitation in light of the unexpected discovery that 95% of the inorganic carbon and 50% of the conductivity is removed.

The results of these batch studies were verified by passing retort water through packed columns of spent shale. Similar reductions in organic carbon and inorganic carbon and increases in pH were observed. In addition, the color of the retort water changed from brown to yellow on passage through the column. A difference spectrum between the untreated water and column effluents taken over the visible and ultraviolet wavelengths shows two separate regions where adsorption has taken place (Fig. 1). One is a broad, deep peak showing almost complete removal of a component or components with a maximum at 390 nm, which is the change responsible for the color change. Anothe peak in the ultraviolet around 215 nm indicates that other components may also be removed by the column. Further work will be done to identify the compounds responsible for these adsorption changes.

The simultaneous increase in pH and large decrease in inorganic carbon has important and immediate applications to the treatment of retort water. Carbonate alkalinity must be reduced in any treatment sequence designed to upgrade this water. These results indicate that a packed column of spent shale can be used in combination with a steam stripper to remove ammonia and carbonate alkalinity from the water. The increase in pH would enhance the removal of ammonia in the stripper. The nearly complete reduction of carbonate alkalinity through the spent shale column would allow the use of a smaller stripping tower. This represents a significant advance in the treatment technology for retort water, and it will considerably reduce the cost of retort water treatment.
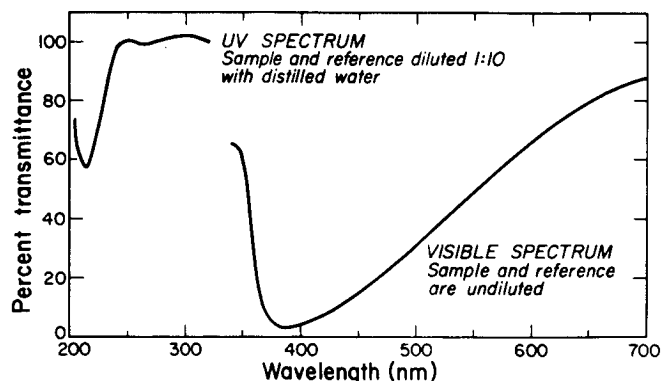


Fig. 1. UV and visible difference spectra. Sample was 150-ton retort water and reference was the effluent of a 50 cm column packed with S-17 spent shale which was fed 150-ton retort water. Adsorption in this spectrum indicates the presence of compounds that have been removed by the column.
(XBL 795-1595)

PLANNED ACTIVITIES FOR 1979

We will continue batch studies in order to generate adsorption isotherms that will be used to identify the best adsorbers, study the effect of pH and temperature on the process, and determine the contact time necessary to reach equilibrium. We plan to measure some of the relevant physical variables such as pore volume, surface area, and carbon content of the shale. Work will also begin on oil and grease removal, a pretreatment required to prevent fouling of the columns. In cooperation with other groups in the Oil Shale Project, we will develop methods of fractionating and identifying the organic solutes in the retort waters so that we can obtain information about the specificity with which particular compounds or classes of compounds are removed from solution by spent shale. After the adsorption process is developed, we will use it in series with biological processes such as trickling filters, activated sludge and anaerobic fermentation to remove organics from retort water.

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# Effect of Retort Water on Attached Microorganisms

## P. P. Russell, A. J. Horne, and J. F. Thomas

INTRODUCTION

Production of synthetic crude from oil shale
generates from 0.10 to 22 barrels of water
per barrel of oil, depending on the specific
process used. This water, referred to as retort
water, originates from combustion, mineral de-
hydration and from groundwater intrusion (in
situ processes only). The organic content
of retort water may reach 3% while inorganic
concentrations of as much as 5% are typical.
The principal inorganic components of the waste-
water are ammonium, sodium, and bicarbonate, with
lesser but significant amounts of thiosulfate,
chloride, sulfate and carbonate.

The goal of this project is to investigate
the probable effects of accidental or intentional
discharge of retort water on attached micro-
organisms (aufwuchs) and caddis fly larvae
in streams of the oil shale region. Aufwuchs
are sensitive indicators of the effect of a
pollutant on the food chain. The aufwuchs
community typically consists of an attached
mat of algae, protozoa, bacteria, fungi, and
some associated metazoans. The approach used
was to employ laboratory scale model streams
containing standardized growth surfaces upon
which aufwuchs communities could develop.
This program was initiated in 1977 and is funded
by the Laramie Energy Technology Center (LETC).
In 1977 four mutually isolated, parallel model
streams, shown in Fig. 1, were constructed.
These streams were used to study the effect
of retort water on aufwuchs. This phase of
the program is discussed here.

ACCOMPLISHMENTS DURING 1978

Two oil shale retort waters were studied.
One sample came from a combustion run of Laramie
Energy Technology Center's (LETC) 150-ton retort

facility (150-ton retort water). The other
was produced during the Rock Springs Site 9
true in situ oil shale processing experiment
(Omega-9 water) near Rock Springs, Wyoming.[1]
These retort waters are not necessarily
representative of waters which may be produced
during other oil shale processing experiments,
and the results obtained are strictly indicative
of these waters only. Nevertheless, probable
aufwuchs responses from the retort waters of
future full scale oil shale processing can
be estimated using this methodology.

Five experimental runs were performed using
Omega-9 water, Omega-9 water filtered through
a 0.4 μm membrane (2 runs), 150-ton retort
water, and an ammonium carbonate solution.
Development and metabolism of aufwuchs on
initially clean growth surfaces in the riffles
of each stream were measured on the third, sixth
and ninth day of each experiment. Assays of
total solids, percent volatile solids, chlorophyll
a, photosynthesis, respiration and adenosine
triphosphate (ATP) were performed. The response
of caddis fly larvae, Gumaga nigricula and
Dicosmoecus sp., were confined to screened
cages in the lower pools of each stream and
their survival monitored.

Preliminary analysis of the results indicates
that these effluents produce the greatest effect
on the percent volatile solids of the aufwuchs.
This response is typically illustrated by the
results from runs using Omega-9 water (Fig. 2).
The increase in percent volatile solids with
retort water probably results from a reduced
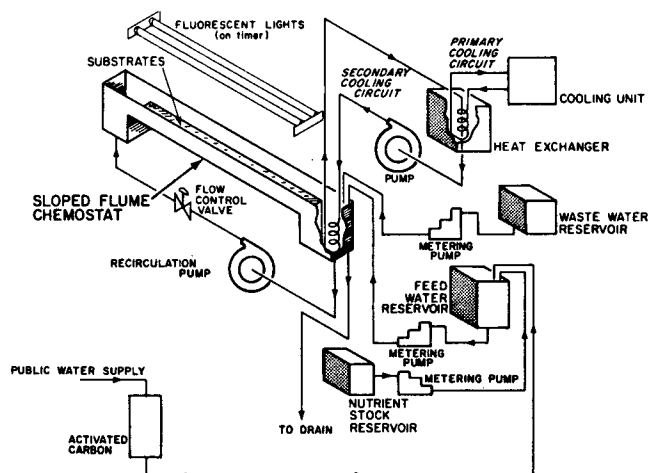contribution of diatoms to the aufwuchs community.
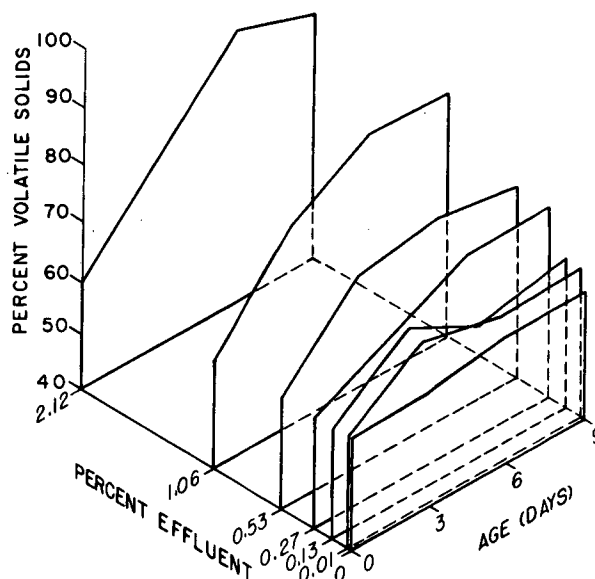


Fig. 1. Model stream schematic. (XBL 779-1907A)



Fig. 2. Aufwuchs percent volatile solids vs.
Omega-9 water dilution and growth
period. (XBL 7811-12618)

Diatoms possess a silica shell or frustule which remains as a solid when the organic matter of the aufwuchs sample is volatilized. The fraction of aufwuchs comprised by green algae when retort water is present typically increases (Table 1). It is likely that the contribution of bacteria to the aufwuchs biomass also increases with the availability of retort water organics, although this fact was not confirmed directly. The increase in percent volatile solids was less pronounced when ammonium carbonate was tested alone.

Other significant results from preliminary analysis of the data suggest increased total biomass at low dilutions of retort water and decreased biomass at concentrations above about 1% retort water. This indicates that the stimulation by low effluent levels is supplanted by toxic effects at higher levels. Additionally, the ratio of gross photosynthesis to respiration tends to decrease with increasing retort water loadings. Evidently, the contribution of the photosynthesizing primary producers diminishes when retort water is present.

The concentrations of retort water examined had no significant effect on the caddis fly larvae. However, the sensitivity of Dicosmoecus sp. to ammonium carbonate (the only run in which it was employed) was more pronounced than that of G. nigricula. Perhaps a response to retort water would have been observed with Dicosmoecus if it had been available for the other experimental runs.

The consequence of shifts of species dominance in the streams of the oil shale region is controversial at this time. Aufwuchs is an important component of energy input to the food web. It is known that many insect species which graze on aufwuchs are quite selective with respect to palatibility, caloric value and availability of the organisms in their diet. These insect grazers are in turn food for higher forms of aquatic life of economic importance to man, i.e., trout. Thus, there is significant potential for perturbations at the base of the food chain to be propagated widely.

PLANNED ACTIVITIES FOR 1979

Analysis of the data will be completed and published early in 1979. Confirmation of the results from this project must be obtained by use of the methodology in the field with oil shale related effluents. Valuable information could be obtained by applying higher concentrations of retort water to the model streams, as well as by examining other types of industrial wastes.

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Table 1. Community composition.

| | | Volume Percent | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Navicula sp 1 | Navicula sp 2 | Navicula sp 3 | Navicula sp 4 | Nitschia | Diatoms | Closteridium | Microspora | Zygnema | Unid. Green Alga | Green Algae |
| Omega-9 Water | 0 | 56 | 1 | 0 | 41 | P | 98 | 2 | 0 | P | P | 2 |
| | 1.06% | 15 | 9 | 0 | 0 | 21 | 46 | 47 | 0 | P | 7 | 54 |
| Filtered Omega-9 Water | 0% | 0 | 34 | 0 | 0 | 0 | 34 | 64 | 0 | P | 1 | 66 |
| | 2.12% | 0 | 31 | 0 | 0 | 0 | 31 | 66 | 0 | P | 3 | 69 |
| 150 Ton Retort Water | 0% | 62 | 5 | 1 | 25 | 6 | 99 | P | 0 | 0 | P | 1 |
| | 0.67% | 0 | 0 | 0 | 0 | 40 | 40 | 51 | 0 | P | 8 | 60 |
| Ammonium Carbonate | 0mM | 43 | 18 | 0 | 36 | 7 | 95 | P | 1 | P | 3 | 5 |
| | 4mM | 0 | 26 | 0 | 13 | 44 | 83 | 1 | 0 | P | 15 | 17 |

P = Present but less than 1%.

# Potential Toxicants from In Situ Oil Shale Processing

*M. J. Kland and J. P. Fox*

INTRODUCTION

Increasing interest in in situ oil shale
retorting as a means of augmenting our domestic
fuel supplies raises the inevitable question
of the potential for environmental and health
impacts of this technology.

Consideration of possible deleterious
environmental effects include - though they
are not necessarily confined to - gaseous and
particulate emissions to the atmosphere,
particulate fallout to the ground and onto
vegetation, and the consequent contamination
of ground and surface waters.

Gases such as CO, $SO_2$, $NH_3$ and $H_2S$, which
are known to be toxic to both plants and animals,
are among the volatile emissions from in situ
oil shale retorting. A variety of potentially
toxic or carcinogenic hydrocarbons have been
identified among the organic pyrolytic products
emitted.[1]

The handling of raw shales presents the
usual occupational respiratory hazards of
exposure to mineral dusts, including silicates,
and adsorbed or occluded toxic trace metals.
Contact with the kerogen and bitumen, which
constitute the organic fraction of raw shale
and contain possible oncogenic substances,
is a further occupational hazard which will
need to be addressed in greater depth. (See
Ref. 1 for a number of excellent industrial
hygiene references dealing with similar problems.)

Product oils collected in the retorting
process contain a variety of hazardous substances:
irritants capable of producing serious contact
dermatites, sensitizers and carcinogens. Among
the oncogenic (tumorigenic) organic compounds
identified are: benz(a)pyrene, benz(a)anthracene,
other pyrenes, chrysenes and dibenzacridine(s).[2]

Residues from retorting include spent shale
with concomitant dust and trace metals, as well
as potential organic toxicants and carcinogens
which may condense out on retort surfaces.

Although there are significant industrial
hygiene and air pollution control problems
connected with in situ oil production technology,
the most serious environmental and public health
concerns stem from process-related waters:
their control and re-use, and the potential
impact of the technology on increasingly scarce
water resources.[3] The remainder of this report
will consider this aspect of the environmental
problems anticipated in the event of large-
scale in situ oil shale development.

Waters associated with in situ oil shale
retorting are a major byproduct of this technology.
They originate from combustion, dehydration
of occluded and bound waters of shale minerals,
and injection water or steam associated with
the retorting process. In addition, seepage
of ground water occurs into the retorted zones
(backflood water).

Waters derived from the in situ oil shale
retorting process are heavily contaminated
with organic and inorganic constituents.[4]
They are generally akaline (ph 8-9.5) with
primarily polar organic constituents (organic
acids, amines, N-heterocyclics and organo oxygen
and sulfur compounds). Inorganic anions include
$HCO^3$, $CO_3$, $F^-$, $S_2O_3$, SCN and $SO_4$; principle
dissolved cations are Na, $NH_4$, Mg, Zn, Fe,
and amphoterics (Al, Si) which exist as complex
anions under alkaline conditions. Trace elements
of environmental concern include As, Hg, Se,
Mo and B.

In addition to their own specific toxic
potential for eco-systems, the hetero-organics
may increase the mobilities of certain of the
toxic trace elements (Cu, Cd, As, Se, F) by
virtue of their complexing and chelating powers.[5]
It is not unusual for metals in organometallic
form to exhibit enhanced toxicity toward fauna
and flora because they may be more readily
assimilated than the parent inorganic ions.
Witness the far greater toxicity to fish and
mammals of methyl and dimethyl mercury than
the free metal or its relatively insoluble
salt, $Hg_2Cl_2$.[6]

The purpose of this project is to identify
specific organic and organometallic compounds
in waters, oils and gases from in situ oil
shale processes and to assess their environ-
mental significance. The program was initiated
in October 1978 and is funded by the Department
of Energy.

ACCOMPLISHMENTS DURING 1978

A program has been initiated to determine
organic and organometallic components in oils,
waters and gases produced during oil shale
retorting. A variety of analytical techniques,
including Zeeman atomic absorption spectroscopy
(ZAA), gas chromatography/mass spectrometry
(GC/MS), high performance liquid chromatography
(HPLC) thin layer chromatography (TLC) and UV-
visible spectrometry, are being used to identify
specific components.

Preliminary solvent extractions and analyses
of shale waters from two sources have indicated
the presence of a number of organonitrogen
heterocyclics, phenols, organic thio derivatives,
carboxylic acids and neutral hydrocarbons.
Interestingly, x-ray fluorescence analysis
of these extracts has also revealed the presence
of As, Se, Zn and other metals.

Further separations and identifications
are in progress, using GC-MS, UV-Vis spectro-

photometry, XRF and ZAA for metals. In addition to organic extraction techniques, we are experimenting with steam distillation in an alternative separation method. Ultimately, TLC and HPLC will also be used for the separation and confirmation of both the organic isolates and organometallics.

## PLANNED ACTIVITIES FOR 1979

Techniques to measure organics and organo-metallics in complex aqueous matrices will be developed and applied to a range of retort waters. Spectrophotometric studies of interactions of pure heterocyclics with one or more of the trace metals will be conducted. A synthetic model organometallic compound will be used to gain further insight into the state in which metals exist in the organic fraction.

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# Intercomparison Studies of Oil Shale Materials

J. P. Fox, F. Asaro, and R. D. Giauque

## INTRODUCTION

Reliable chemical characterizations of oil shale materials have been difficult to obtain because of the lack of adequate standards and limitations of many available analytical methods. Concentrations of many constituents fall outside the recommended ranges for many methods, and chemical interferences produce inaccurate results.

The purpose of this investigation is to develop oil shale standards and to use these materials to identify/develop reliable analytical methods for the characterization of oil shale materials. This program was initiated in 1976 and is funded by the Laramie Energy Technology Center (LETC) and DOE's Division of Fossil Fuel extraction. The program is a collaborative effort with LETC, Battelle Pacific Northwest Laboratory and the Colorado School of Mines. Each collaborator prepared a series of standard reference materials which were distribted to various laboratories for analysis in 1977. The resulting data have been interpreted and recommendations advanced for suitable analytical methods for oil shale materials. This phase of the program is outlined below.

## ACCOMPLISHMENTS DURING 1978

Fifty kilograms of 3 oil shales, 7 spent shales, 12,500 gallons of retort water and 5 liters of 2 oils were homogenized, split and submitted to various laboratories for elemental analyses. A range of water quality parameters was determine in the retort water.

The results of the analysis of one oil shale standard are shown in Table 1. These data were analyzed to determine method/laboratory performance. Partial results of the performance analysis for each type of material are summarized in Table 2. This analysis indicated that reliable measurements of elemental abundances in raw and spent oil shales can be obtained using neutron activation analysis, x-ray fluorescence spectrometry and atomic absorption spectroscopy if laboratories are chosen that do careful work. Chemical techniques are limited by a number of interferences and should not be used unless careful methods development preceeds analysis.

Less satisfying results were obtained for the oil and water. The statistics summarized in Table 2 indicate that the coefficient of variation for the normalized means was 26% for the oils and 33% for the waters compared with 9% for the solids. This large variation for the oils and waters is due to the low levels of many constituents and to uncorrected chemical interferences.

Significant analytical problems were encountered with the retort water. Large deviations were obtained for many elements (Al, P, Pb, Hg, Sr, Si, Cd) and water quality parameters (COD, phenols, CN, organic nitrogen, $PO_4$).

Table 1. Elemental composition of Anvil Points raw oil shale prepared by LBL, Raw 1B (ppm).

| | Neutron Activation Analysis | | | | X-ray Fluorescence Spectrometry | | | | | Other | | Best value[1] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (D-1) | (D-2) | (A)(2) | (O)(1) | High energy (D) | High energy (A-1)(2) | High energy (J)(3) | Low energy (A-2)(1) | Low energy (D) | (A)(3) | (J) | |
| Al (%) | - | - | 3.83±0.12 | 4.04±0.19 | 38±3 | - | - | 4.0±0.2 | 3.88±0.34[a] | - | - | 3.9±0.1 |
| As | 54±1 | 62±1 | 45±4 | 39±1 | - | 37±1 | 40±9 | - | - | - | 33±3[a] | 47±10 |
| B | 540±50 | - | - | - | - | - | - | - | 108±11[g] | - | - | (108±11) |
| Ba | - | - | 498±26 | 479±19 | - | - | 520±36 | - | - | - | - | 495±27 |
| Br | 0.52±0.16 | - | - | - | - | <1.5 | 0.55±0.01 | - | - | - | - | 0.55±0.02 |
| Ca (%) | 8.25±0.6 | - | 10.3±0.5 | 9.41±0.12 | 10.5±0.8 | - | 11±1 | 9.2±0.5 | 10.0±0.5[a] | - | - | 9.5±0.9 |
| Cd | - | - | - | - | - | - | - | - | - | 0.72±0.07[b] | - | 0.72±0.07 |
| Ce | 46±2 | - | 44±2 | 41.2±0.6 | - | - | - | - | - | - | - | 42±2 |
| Cl | - | - | <830 | - | - | - | - | - | - | - | - | (<830) |
| Co | 9.3±0.3 | 8.8±0.1 | 9.18±0.29 | 8.56±0.09 | - | <31 | - | - | - | - | - | 8.7±0.3 |
| Cr | 45±1 | 49±1 | 37±2 | 33.1±0.8 | - | - | - | - | - | - | - | 41±7 |
| Cs | - | - | 4.46±0.33 | 4.40±0.10 | - | - | - | - | - | - | - | 4.4±0.1 |
| Cu | - | - | - | <98 | 43±4 | 40±3 | 34±3 | - | - | 40±4[b] | - | 39±4 |
| Dy | - | - | 2.48±0.13 | 2.13±0.14 | - | - | - | - | - | - | - | 2.32±0.25 |
| Eu | - | 0.59±0.03 | 0.63±0.02 | 0.59±0.01 | - | - | - | - | - | - | - | 0.60±0.02 |
| F | - | - | - | - | - | - | - | - | - | - | 990±20[g] | (990±20) |
| Fe (%) | 2.41±0.05 | 2.29±0.05 | 2.21±0.06 | 2.16±0.02 | 2.2±0.2 | 2.18±0.09 | 2.10±0.04 | 2.1±0.1 | 2.24±0.31[a] | - | - | 2.2±0.1 |
| Ga | - | - | - | - | 10.1±1.2 | 9.8±1.8 | 6.5±0.7 | - | - | - | - | 7.7±2.0 |
| Ge | - | - | - | - | - | <2.4 | - | - | - | - | - | (<2.4) |
| Hf | 1.7±0.1 | - | 1.72±0.14 | 1.68±0.04 | - | - | - | - | - | - | - | 1.69±0.04 |
| Hg | 0.06±0.01 | - | <0.18 | - | - | <4 | - | - | 0.086±0.005[a] | 0.077±0.008[b] | - | 0.08±0.01 |
| In | - | - | <0.18 | - | - | - | - | - | - | - | - | (<0.18) |
| Ir | - | - | <0.01 | - | - | - | - | - | - | - | - | (<0.01) |
| K (%) | 1.83±0.19 | - | 1.79±0.14 | 1.77±0.06 | 1.67±0.12 | - | - | 1.7±0.1 | 1.61±0.11[a] | - | - | 1.73±0.08 |
| La | 21.2±0.5 | 20.2±0.4 | 20.8±0.7 | 23.4±0.3 | - | - | - | - | - | - | - | 22±10 |
| Lu | 0.26±0.03 | - | 0.19±0.01 | 0.214±0.008 | - | - | - | - | - | - | - | 0.21±0.04 |
| Mg (%) | - | - | 3.5±1.6 | 3.6±0.09 | - | - | - | 3.5±0.2 | 3.52±0.10[a] | - | - | 3.5±0.1 |
| Mn | - | - | 343±12 | 334±2 | 350±30 | 341±21 | 300±8 | - | 395±70[a] | - | - | 333±31 |
| Mo | - | - | 20±2 | 19±1 | 21±2 | - | 20±2 | - | - | - | 19±2[c] | 20±1 |
| Na (%) | 1.54±0.01 | 1.58±0.01 | 1.56±0.04 | 1.53±0.01 | - | - | - | 1.7±0.1 | - | - | - | 1.55±0.02 |
| Nb | - | - | - | - | - | - | 5.7±0.1 | - | - | - | - | (5.7±0.1) |
| Nd | - | - | 19±4 | 14±3 | - | - | - | - | - | - | - | 16±4 |
| Ni | 25±2 | 26±1 | 21±4 | <36 | 23±3 | 20±4 | 29±1 | - | - | - | - | 27±3 |
| Pb | - | - | - | - | 24.5±0.3 | 24±2 | 23±1 | - | - | 23±3[b] | - | 24±1 |
| Rb | 76±5 | 74±1 | 85±8 | 74±3 | 79±6 | 74±2 | 82±1 | - | - | - | - | 77±4 |
| Sb | 2.0±0.1 | 1.99±0.10 | 2.1±0.1 | 1.90±0.07 | 2.2±0.5 | 2.1±0.7 | - | - | - | - | - | 2.0±0.1 |
| Sc | 6.8±0.1 | 7.0±0.1 | 7.0±0.07 | 5.93±0.05 | - | - | - | - | - | - | - | 6.3±0.5 |
| Se | 2.6±0.3 | 2.6±0.1 | 6.47±0.20 | 2.38±0.30 | - | - | - | - | - | - | - | 2.6±0.2 |
| Si (%) | - | - | - | - | 15.0±1.0 | - | - | 15.0±0.8 | 14.9±1.2[a] | - | - | 15.0±0.8 |
| Sm | 3.6±0.1 | 3.5±0.1 | 3.08±0.12 | 3.19±0.07 | - | - | - | - | - | - | - | 3.3±0.2 |
| Sr | 840±50 | 740±15 | - | 683±29 | - | 698±19 | 798±4 | - | 720±60[a] | - | - | 789±61 |
| Ta | 0.55±0.02 | - | 0.46±0.02 | 0.47±0.04 | - | - | - | - | - | - | - | 0.50±0.05 |
| Tb | 0.37±0.04 | - | 0.40±0.07 | 0.36±0.02 | - | - | - | - | - | - | - | 0.36±0.02 |
| Th | 7.0±0.1 | 7.0±0.2 | 6.70±0.26 | 6.18±0.07 | - | 6.8±1.7 | - | - | - | - | - | 6.5±0.3 |
| Ti (%) | - | - | 0.16±0.05 | 0.17±0.03 | 0.17±0.03 | 0.18±0.02 | - | 0.16±0.01 | 0.17±0.03[a] | - | - | 0.17±0.01 |
| U | - | - | 4.10±0.16 | 3.63±0.20 | - | - | - | - | - | - | - | 3.9±0.3 |
| V | - | - | 107±24 | 92±5 | - | - | - | - | - | - | - | 93±11 |
| W | - | - | - | - | - | - | - | - | - | - | - | - |
| Y | - | - | - | - | 12±2 | 13±1 | 12±1 | - | - | - | - | 12±1 |
| Yb | 1.6±0.1 | - | 1.38±0.05 | 1.31±0.03 | - | - | - | - | - | - | - | 1.3±0.2 |
| Zn | 70±6 | 65±1 | - | 75±3 | 69±7 | 67±3 | 63±2 | - | - | - | - | 66±4 |
| Zr | - | - | - | - | 56±8 | - | 49±3 | - | - | - | - | 50±5 |

A = Lawrence Berkeley Laboratory,  D = Battelle Pacific Northwest Laboratory,  J = University of Colorado,
O = Lawrence Livermore Laboratory,  a = atomic absorption spectroscopy,  b = Zeeman atomic absorption spectroscopy,  c = colorimetric,
d = fluorometric,  e = delayed neutron,  f = gamma-ray spectrometry,  g = plasma emission spectroscopy.

[1] The following rules were used to determine best values: (1) The smallest upper limit is reported; (2) A range is reported if the coefficient of variation is greater than 100%; (3) Best values based on a single measurement are enclosed in parenthesis; (4) Best values based on two or more measurements are weighted averages computed following rejection of outliers. The reported errors are the larger of one standard deviation computed from the reported replicates or the smallest recorded analytical error.

Table 2. Normalized statistics for oil reference materials

| | Normalized average | Coefficient of variation | Uncertainty in coefficient of variation |
|---|---|---|---|
| **RAW OIL SHALE** | | | |
| NAA (D-1) | 1.04 ± 0.10 | 10% | 1.4% |
| NAA (D-2) | 1.04 ± 0.10 | 10% | 1.8% |
| NAA (A) | 1.02 ± 0.08 | 7.6% | 1.0% |
| NAA (O) | 0.97 ± 0.06 | 6.6% | 0.80% |
| XRF (D) | 1.02 ± 0.11 | 11% | 2.0% |
| XRF (A-1) | 0.98 ± 0.13 | 14% | 2.7% |
| XRF (A-2) | 1.00 ± 0.05 | 4.9% | 1.3% |
| XRF (J) | 0.98 ± 0.09 | 9.1% | 1.7% |
| AA (D) | 1.02 ± 0.08 | 7.6% | 1.8% |
| **SHALE OIL** | | | |
| NAA (D-2) | 1.27 ± 0.46 | 36% | 7.5% |
| NAA (O) | 0.92 ± 0.16 | 17% | 3.5% |
| XRF (D) | 0.92 ± 0.16 | 17% | 4.7% |
| XRF (A) | 1.26 ± 0.31 | 25% | 7.4% |
| XRF (J) | 1.13 ± 0.38 | 34% | 9.2% |
| **RETORT WATER** | | | |
| NAA (A) | 0.97 ± 0.22 | 23% | 4% |
| NAA (B) | 1.08 ± 0.34 | 31% | 9% |
| NAA (C) | 0.95 ± 0.17 | 18% | 4% |
| NAA (D) | 0.94 ± 0.19 | 20% | 5% |
| NAA (O) | 0.92 ± 0.19 | 20% | 4% |
| XRF (A) | 0.96 ± 0.21 | 22% | 4% |
| XRF (D) | 1.02 ± 0.31 | 30% | 8% |
| SSMS (E) | 1.30 ± 0.79 | 61% | 9% |
| OES (F) | 0.96 ± 0.49 | 51% | 11% |
| PES (D) | 0.88 ± 0.25 | 28% | 6% |
| AA | 1.03 ± 0.17 | 17% | 3% |
| OTHER | 1.15 ± 0.80 | 70% | 15% |

Letters A-J designate laboratories; NAA = neutron activation analysis;
XRF = x-ray fluorescence spectrometry; AA = atomic absorption spectroscopy;
SSMS = spark source mass spectrometry; OES = optical emission spectroscopy;
PES = plasma emission spectroscopy.

The concentration of many elements was near the detection limit of instrumental methods. Acidification, which is conventionally used as a pretreatment step for metal analyses, resulted in the precipitation of elemental S and carboxylic acids which acted as an adsorbent for some elements, interfered with most analytical measurements, and resulted in an inhomogeneous sample. The performance of x-ray fluorescence, neutron activation, plasma emission and atomic absorption spectroscopy on the water was significantly better than that of spark source mass spectrometry, optical emission spectroscopy and other methods.

The study of water quality parameters demonstrated that standard methods, such as ASTM or EPA methods, cannot be used to accurately measure many of these parameters in these types of waters. The following methods were found to give incorrect results when used to analyze retort waters: (1) $Hg(NO_3)_2$ titration and Technicon AutoAnalyzer methods for Cl; (2) titrimetric method without pretreatment for $S^=$; (3) gravimetric method for solids; (4) permanganate oxidation method for COD; (5) indirect method for TOC. Some existing chemical methods for the measurement of alkalinity, $SO_4$, inorganic C, Na, SCN, As, and total S and methods developed in this work for $CO_3$, $HCO_3$ and Cl may be adequate for routine analyses following limited additional laboratory testing.

PLANNED ACTIVITIES FOR 1979

The intercomparison studies initiated for oil shale materials will be extended to other synfuels including tar sands and coal gasification. Also additional work will be completed on oil shale retort waters. Other waters will be studied and work initiated to resolve the large number of chemical interferences found for standard analytical methods.

# Advances in Soft X-Ray Fluorescence Spectrometry
## for Oil Shale Analyses

### S. Flexser, H. R. Bowman, and J. M. Neil

## INTRODUCTION

The low energy dispersive x-ray spectrometer developed at LBL[1] has previously been used to determine the abundances of the major rock-forming elements in a variety of rock samples. Powdered samples are fused with a low-melting matrix ($LiBO_2$) to produce amorphous glass discs for analysis.

The purpose of this study was to apply this technique to the analysis of oil shale, which contains considerable volatile material, and to expand the suite of elements measured to include P, S, and Cl, which are generally minor constituents of rock samples. This involved the resolution of some particularly difficult technical problems, including sample crystallization on cooling, spectral background determinations, and loss of organics during fusion.

## ACCOMPLISHMENTS DURING 1978

In order to determine the spectral backgrounds beneath the P, S, and Cl peaks, it was first necessary to evaluate the mutual interference of these adjacent peaks. Figure 1 shows the spectrum of a standard used in analyses of oil shales, excited by AgL$\beta$ x-rays. Peak interferences were studied using samples of individual elements as well as "blank" samples - discs of fused matrix alone. Past attempts to prepare such samples had failed due to crystallization on cooling, but this problem was circumvented by combining boric acid, in ratios up to 2:1, with the $LiBO_2$ matrix. This enabled us to observe the effect of crystallization on the x-ray spectra of blank discs. Figure
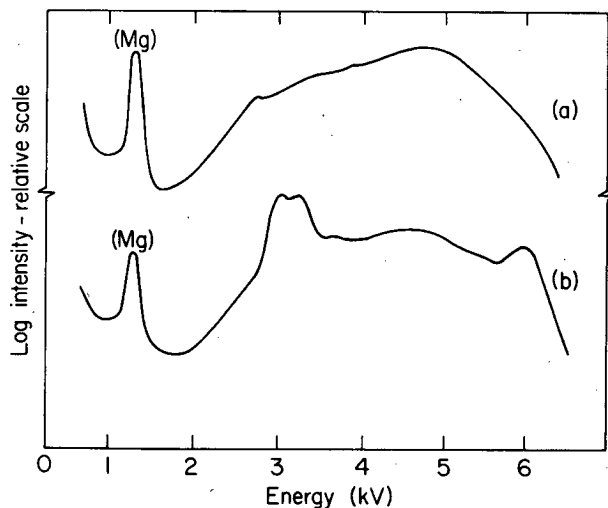


Fig. 1. X-ray spectrum of standard used in analysis of oil shales. Peaks of P, S, and Cl are shown. Exciting radiation is AgL$\beta$ x-ray resulting in peak to right of Cl. (XBL 791-241)
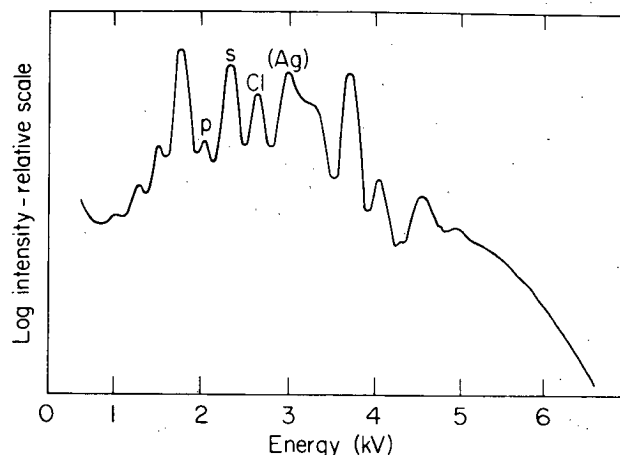


Fig. 2. X-ray spectra of blanks of identical composition with (a) no apparent crystallization and (b) considerable crystallization. Anomalous broad peaks in (b) are presumed diffraction peaks. Exciting radiation is MgK$\alpha$ x-rays, resulting in sharp peaks to the left. (XBL 791-240)

2 compares the x-ray spectrum for an amorphous blank disc (a), with that of a blank disc which crystallized considerably during cooling (b). Both samples were excited by MgK $\alpha$ x-rays, resulting in the sharp peaks shown. (Excitation by other radiation - e.g., by AgL$\beta$ x-rays - results in additional anomolous peaks and distortations of the spectrum which can interfere with fluorescence peaks. However, these anomalies are most apparent with MgK $\alpha$ excitation.) The anomalous peaks in (b) are presumed to be diffraction peaks resulting from crystallization. We hope to verify this by correlating these peaks with specific reflecting planes in the crystallized Li-borate compounds using diffraction techniques.

This investigation indicated that boric acid can effectively suppress crystallization during cooling of samples fused with a $LiBO_2$ matrix, and that such crystallization is likely to result in diffraction of x-rays.

## PLANNED ACTIVITIES FOR 1979

The techniques developed to analyze oil shales will be applied to a range of samples to develop geochemical and environmental information.

## REFERENCE

A. J. Herbert, and K. Street, Jr., "A nondispersive soft x-ray fluorescence spectrometer for quantitive analysis of the major elements in rocks and minerals," LBL 1616 (1973).

# Methods for the Measurement and Analysis of Dissolved Gases in Complex Aqueous Mixtures

## S. P. Lubic and A. S. Newton

## INTRODUCTION

During the past year, methods were developed for the measurement and analysis of dissolved gases in water from wells and artesian springs and oil shale retort waters. In each method the water samples are degassed on a vacuum system and the evolved gas mixtures fractionated and collected in a series of low temperature traps. The amount of gas collected in each fraction is measured and the gas is transferred to glass sample bulbs for analysis by mass spectrometry.

## ACCOMPLISHMENTS DURING 1978

### Dissolved Gases in Well and Spring Waters

A method was developed to measure dissolved gases in well and spring waters without atmospheric contamination of the sample. A number of one liter stainless steel sample containers and associated valves and fittings were tested for vacuum tightness. After evacuating the sample containers, 20.0 torr of an internal standard gas mixture was added to each sample container. The gas mixture consisted of $^3He$, Kr and $CF_4$. The $^3He$ was used as an internal standard for the measurement of $^4He$ dissolved in the water. Kr was used to measure the efficiency of gas recovery from the water and sample container, and $CF_4$ acted as a carrier for gas transfer in the vacuum system and provided a suitable expansion volume for the water in the sample container. Atmospheric contamination of the sample was prevented by alternately evacuating and purging the sample line with $CF_4$ before water samples were aspirated into the sample containers.

The samples were transferred to the vacuum system by means of stainless steel lines connected to a two liter collection flask fitted with a large cold finger to prevent water contamination of the vacuum system (Fig. 1). The traps and two liter vessel were evacuated prior to sample introduction. The water was allowed to flow into the collection flask and then degassed. Evolved gases were collected in a series of traps. After degassing was completed the traps were isolated from the collection flask and vacuum manifold, connected to a Toepler pump, allowed to warm and the evolved gases transferred to a thermostatted gas buret. The gases were then transferred by mercury displacement from the gas buret into evacuated demountable sample bulbs and analyzed with a CEC model 21-103 mass spectrometer. Gas standards were run to determine mass fragmentation patterns and sensitivities. Analyses of various gas fractions were performed and the water basis determined. Results from a number of samples taken at the Hanford reservation in Washington are presented in Table 1.

### Inorganic Carbon in Retort Waters

This method was developed to check the accuracy of the usual method which involves the evolution of $CO_2$ from an acid treated column of quartz chips maintained at 150°C followed by IR analysis of evolved $CO_2$. Our method uses acid addition to shift the $H_2CO_3$, $HCO_3$, $CO_3$ equilibrium such that $H_2CO_3$ is the predominant component. At low pH the solubility of $H_2CO_3$ is low and $CO_2$ will be evolved from solution. As the $CO_2$ is removed from solution, the equilibrium is further shifted until essentially all the
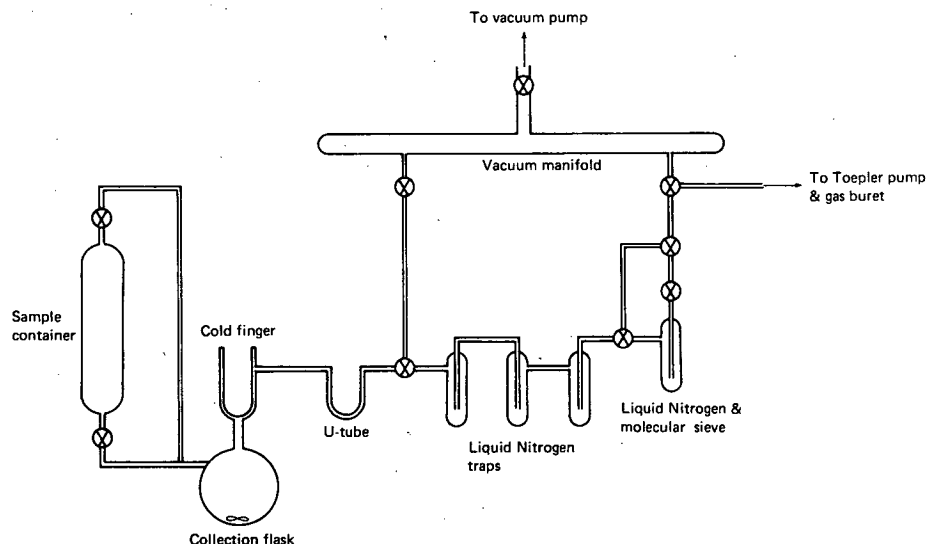


Fig. 1. Experimental setup used to measure dissolved gases in well and spring water. (XBL 791-245)

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Table 1. Data summary for water samples for wells and artesian springs.[a]

| Component | Source | | | | | |
|---|---|---|---|---|---|---|
| | DC6 | W1 | SP1 (spring) | W2 | DC6 | DC2 |
| $H_2$ | - | 0.004 | 0.21 | <0.00002 | 0.013 | 0.74 |
| He | - | 0.00027 | 0.00035 | 0.00052 | - | - |
| $O_2$ | 0.015 | 0.11 | 0.32 | 12 | 0.014 | <0.02 |
| $N_2$ | 18 | 12 | 55 | 57 | 11 | 192 |
| Ar | 0.17 | 0.28 | 0.75 | 0.77 | 0.23 | 1.4 |
| $CO_2$ | 0.43 | 1.5 | 1.1 | 1.6 | <0.016 | 0.0054 |
| $CH_4$ | 0.14 | 7.1 | 0.061 | 7.3 | 0.13 | 48 |
| $C_2H_6$ ) | | | | | | 0.01 |
| Higher ) | | Sample DC2 only | | | | |
| Hydrocarbons) | | | | | | <0.001 |

[a]All values reported as ppm on a mole of gas per $10^6$ moles of water basis

inorganic carbon, originally present as $HCO_3$ and $CO_3$, is removed.

Five ml of an oil shale retort water sample were added to a 25 ml long neck, Pyrex flask; the flask was sealed and the contents immediately frozen in liquid nitrogen. One ml of concentrated $H_3PO_4$ was added to the solid sample and the flask connected to the vacuum gas transfer system. The whole system was then evacuated (Fig. 2). The flask was warmed and $CO_2$ was evolved as the $H_3PO_4$ mixed with the sample. The heat was removed and pumping continued until the solution began to freeze. At that point the sample flask and first trap were isolated from the rest of the system. The traps were warmed and the evolved gas transferred with a Toepler pump to a gas buret and analyzed by mass spectrometry. Analytical results for three retort waters are presented in Table 2.
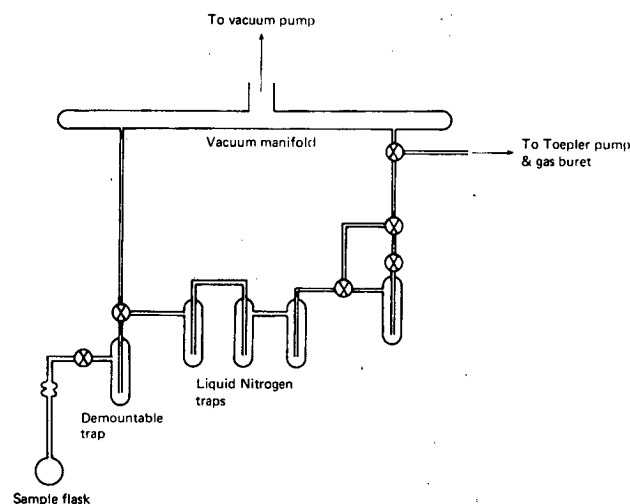


Fig. 2. Experimental setup used to measure $CO_2$ in retort water. (XBL 791-244)

Table 2. Results for three oil shale retort water samples

| Sample | # of analyses | mg/$\ell$ inorganic C[a] |
|---|---|---|
| 150 ton | 3 | 6404 ± 43* |
| S-13 | 2 | 4042 ± 3 |
| S-15 | 2 | 5358 ± 35 |

[a]$\bar{x}$ ± $1\sigma$

The two methods differ primarily in the means of sample preparation and the choice of traps necessary to isolate the components of interest. For the analysis of well samples it was necessary to devise a method to minimize atmospheric contamination in sampling as well as in transferring the sample to the vacuum system. Furthermore, since the amount of gas to be collected was small and the sample volume large, an internal standard was necessary to estimate the amount of gas recovered from the sample. For the analysis of the well samples it was necessary to use several traps to isolate all the components. In the analysis of the shale waste water sample, since evolved carbon dioxide was the only component of interest, the choice of trap was simple. By choosing liquid nitrogen, oxygen and nitrogen were not retained and the subsequent analysis was simpler. Finally, the two methods are general and with a few modifications, for example in the temperature of number of traps, could be applicable to other problems.